

Development of Integrated Catalytic Membrane-Based Unit for Biofuel Production

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ABSTRACT

Flow-through catalytic membrane system for ester production is one of the competitive alternatives to the conventional esterification system. This article presents the development of an integrated reaction/regeneration unit that was established to study the reaction followed by the regeneration step using two consecutive membrane reactor units working alternately. The hypothesis led to continuous ester production with a relatively high average conversion. The esterification reaction conversion of ethylhexanoic acid with ethanol and acetic acid with ethanol using catalytic membrane reactor reached up to 97.7% and 96%, respectively at room temperature after a reaction time of 10 sec, then slowly decreased; this is attributed to the decrease of catalytic membrane efficiency due to water adsorption on active functional groups, making a regeneration step mandatory. The developed unit was used to produce biofuel/biodiesel by esterification of acetic acid and fatty acid with ethanol.

Keywords: Catalytic membrane, esterification, regeneration, integrated pilot unit

INTRODUCTION

Functionalised membranes with catalytic active groups have recently attracted significant attention in chemical production, where the membranes are capable of achieving dual purposes: reaction and separation, where each single process intensifies performance and operation, which will lead to cost effectiveness of the production system. The removal of one or more products in reversible reaction promotes the forward direction by breaking the thermodynamic equilibrium

barrier. Among the merits of membrane catalytic reactors are supra conversion, high productivity and product quality (Mbaraka *et al.*, 2003; Shah *et al.*, 2005; Maria *et al.*, 2006; Sawant *et al.*, 2007; El-Zanati *et al.*, 2011).

Furthermore, the functionalised catalytic membranes containing sulfonated polystyrene grafts have successfully been used as an

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alternative to conventional catalysts that are applied in esterification processes (El-Zanati *et al.*, 2012; Abdallah *et al.*, 2013). A flow-through catalytic membrane reactor describes the concept for continuous heterogeneous reactions, where the catalyst is immobilised in the pores of the membrane. The porous membrane does not perform any separation tasks; it is exclusively used as a microstructure catalyst carrier (Shah *et al.*, 2005; Shi *et al.*, 2013). This type of reactor allows high catalytic activity due to intensive contact between the reactants and catalyst and it provides potentially a narrow residence time (Ozdemir *et al.*, 2006; Westermann & Melin., 2009; Westermann *et al.*, 2009; Buonomenna *et al.*, 2010). Accordingly, functionalised membranes are considered a type of multi microreactors since the reaction actually takes place inside the membrane pores. However, functionalised catalytic membranes have exhibited high catalytic efficiency and great potential for some important reactions, such as esterification, isomerisation, oxidation, hydrogenation, dehydrogenation etc. (Shah & Ritchie., 2005; Shah *et al.*, 2005).

Shah and Ritchie (2005) implanted sulfonic acid groups onto the pore surface of polyethersulfone (PES) microfiltration membrane to catalyse the esterification of ethanol and acetic acid. In a previous study Abdallah *et al.* (2013) made up suitable microfiltration membranes for reaction catalysis, where grafting of sulfonic groups on polyethersulphone membranes was developed to catalyse esterification reactions; the reaction conversion reached more than 90% after 10 sec. Also, El Zanati and Abdallah (2012) investigated the same reaction using a modified grafted membrane by increasing the catalytic efficiency of the membrane up to 33.7% and using a large membrane area, the reaction conversion reached 97% after 10 sec process time. Likewise, in a former study a set of parameters influencing the esterification reaction was conducted (El-Zanati *et al.*, 2011), where the results indicated that increasing the molar ratio increases catalytic efficiency (by increasing styrene percentage in the membrane-grafting step) and the internal surface area of the pores in terms of reaction conversion and productivity.

In a catalytic membrane reactor, the reaction conversion is suddenly increased to maximum value, which is attributed to water adsorption on the sulfonic groups. It then starts to decline slowly, owing to deactivation of the catalytic active sites by the adsorbed water within the membrane pores. Therefore, the membrane becomes progressively saturated; this behaviour creates an optimisation problem; therefore, at optimum time the membrane could be shifted to the regeneration step for further uses (El-Zanati *et al.*, 2012; Abdallah *et al.*, 2013).

Shi *et al.* (2013) studied a novel composite catalytic membrane that was prepared from a sulfonated polyethersulfone and polyethersulfone blend and supported by non-woven fabrics as a heterogeneous catalyst to produce biodiesel from continuous esterification of oleic acid with methanol in a flow-through mode, where an oleic acid conversion was kept at over 98% for 500 hours, running continuously.

The difference between this work and our previous work is the intention to design and develop an integrated catalytic membrane pilot unit for continuous esterification/regeneration steps; in Abdallah *et al.* (2013), the authors studied the polyethersulfone membrane preparation parameters to produce a microfiltration polyethersulfone that could be grafted by catalytic groups and then applied in esterification reaction of ethanol with acetic acid, with the reaction carried out in a small membrane holder with diameter 47mm. In their article, El Zanati and Abdallah (2012) showed how the membrane grafting parameters were studied and the

mathematical model of the grafting polymerisation steps were studied to reach optimum grafting parameters. El-Zanati *et al.* (2011) investigated the parametric study of the esterification reaction of ethanol and acetic acid using a small-sized 47mm catalytic membrane holder, where the membrane was purchased and not prepared in the lab.

The aim of the present work was the development of an integrated catalytic membrane pilot unit for continuous esterification/regeneration. The design was established on using two parallel membrane reactors for esterification/regeneration steps.

EXPERIMENTAL WORK

Design of an Integrated Continuous Esterification System

A conceptual design of an integrated continuous catalytic membrane system used to produce ester was developed. The design approach was based on experimental results and a pre-developed mathematical model that was obtained from previous work (El-Zanati *et al.*, 2011; El-Zanati *et al.*, 2012; Abdallah *et al.*, 2013; El-Zanati *et al.*, 2014). These results revealed that the reaction conversion was increased suddenly and reached maximum value after 10 sec and this lasted for a certain time depending on reaction design parameters. Since the reaction conversion started to slowly decrease with time, this phenomenon was attributed to membrane deactivation due to adsorbed water on functionalised sulfonic active groups. The adsorbed water is accompanied by deactivation of the catalytic membrane efficiency; therefore, membrane regeneration became mandatory to dehydrate the membrane.

The dehydration was conducted by sulfuric acid and it enabled membrane reuse and, consequently, enhanced system cost-effectiveness. The conceptual design principal was based on conducting reaction and regeneration simultaneously. The membrane regeneration was achieved by treating the used membrane with 1N sulfuric acid (acting as water adsorbing agent) at 25°C under 2 bar nitrogen pressure. The regeneration step was stopped when the sulfuric acid concentration left the membrane without changes; this process takes approximately 20 min (El-Zanati *et al.*, 2011). Results of the esterification process obtained from an earlier study (El-Zanati *et al.*, 2011) are illustrated in Fig.1, where is shown the change of reaction conversion with time at the internal pore surface area of 125510 cm². This study also investigated the optimum regeneration time, as shown in Fig.2. Fig.3 exhibits the conceptual design flow sheet; it indicates that the first reactor shifted to functioning as a regenerator when the conversion reached a set point; this point was later determined by feedback on experimental results. The second reactor was then in service and started the reaction until the conversion reached the set point; then it shifted to regeneration, while the reaction was transferred to the first reactor and so on.

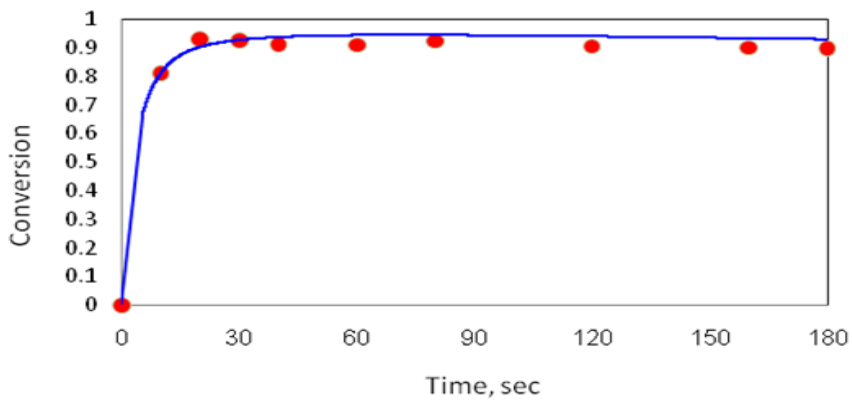


Fig.1: Change of reaction conversion with time (El-Zanati *et al.*, 2011).

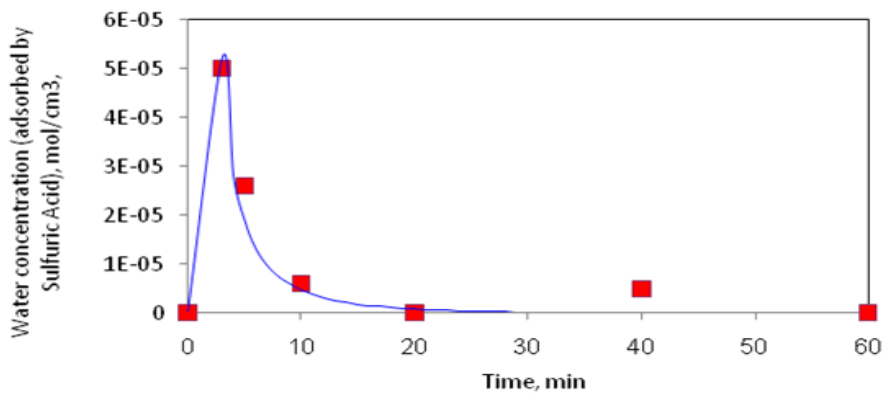


Fig.2: Regeneration time (El-Zanati *et al.*, 2014).

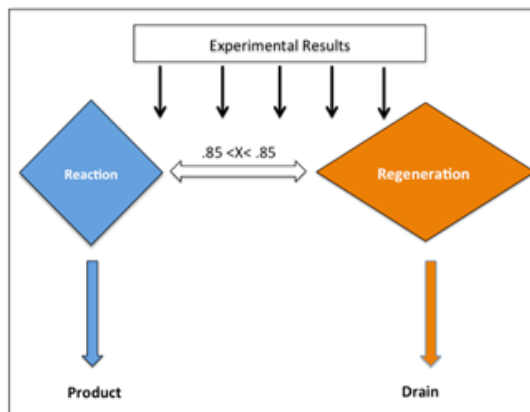


Fig.3: The conceptual design flow sheet.

Process Design

The esterification flow-through process using a catalytic membrane was designed according to previous experimental conditions (El-Zanati *et al.*, 2011; El-Zanati *et al.*, 2012; Abdallah *et al.*, 2013; El-Zanati *et al.*, 2014). The design that was proposed was based on using two reactors working alternately to conduct the esterification reactions (ethanol with acetic acid and ethanol with ethylhexanoic acid) and membrane regeneration. The design depended on some basis on the previous experiment, which rested on the following principles:

1. Asymmetric flat sheet polyethersulfone (PES) membranes of 14.2 cm diameter were prepared by phase-inversion method. The polymer solution was prepared using 16% PES in DMF, 2.5% PEG 400 as polymeric additive (Abdallah *et al.*, 2013).
2. The grafting process of the membranes was conducted by permeating a 1N H₂SO₄ solution through a PES membrane at 60°C under pressure drop of about 2 bars for 1 hour and 12% volume of styrene in toluene was used for 10 minutes at a constant pressure drop of 2 bar and at 25°C. The final step was to terminate the graft through permeation of 1N H₂SO₄ through the membrane for 1 hour at a constant pressure drop of 2 bar and at 25°C (Zanati *et al.*, 2012).
3. Two stainless steel 316L reactors of same size (14.2 cm diameter) were used to carry out the reaction and regeneration.
4. The first reactor worked continuously for 1 hour in reaction step (starting from $t=0$ to $t=1$ hr), then worked 20 min in regeneration step (starting from $t=1$ hr to $t=20$ min, where the total time was 1 hr and 20 min for reaction/regeneration steps).
5. Meanwhile, the second reactor started the reaction step at $t=1$ hr to $t=2$ hr, then started for regeneration to $t=20$ min. This process was performed continuously for 6 hr.
6. The product was collected continuously from each reactor and collected in a holding tank.

The process design depended on parameters that were selected according to the optimum parameters from previous experiments (El-Zanati *et al.*, 2011; El-Zanati *et al.*, 2012; Abdallah *et al.*, 2013) where, the molar ratio of the feed in the esterification reactions were (2:1) ethanol to acetic acid and (5:1) ethanol to fatty acid. The reactions were carried out in membrane reactors with a diameter of 14.2 cm. The reaction temperature was 25°C. The working time in each reactor was 1 hr and the regeneration duration for each reactor was 1 hr, where the two reactors were working in alternately.

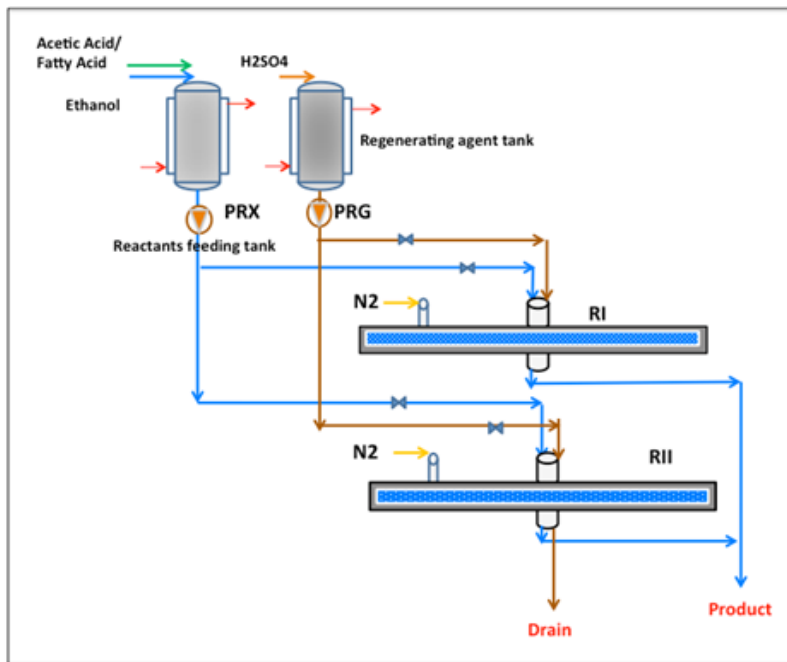


Fig.4: Flow sheet of pilot integrated unit for reaction and regeneration.

Implementation of Integrated Esterification/Regeneration Unit

The basic process design of the pilot unit comprised two reactors and their auxiliaries were manufactured in the workshop of the National Research Centre, Egypt except for the membrane holders that were purchased from Sartorius Company, Germany (Fig.4). The reaction/regeneration unit comprised a feeding tank of stainless steel 316 L, 1 L capacity, which was connected to the first and second reactors by a network of stainless steel pipes (316 L, 1/4" diameter) and valves to facilitate the manoeuvre from reaction step to regeneration step and from one unit to another easily. The feeding vessel had two openings, one for applying nitrogen, used as a blanket and as a support for the feeding step for both steps (reaction and regeneration), and the other for charging either the reactants or regenerating solution.

The reactor (membrane holder) of stainless steel (316 L) and a diameter of 14.2 cm had an upper and lower ticked cover, and the grafted membrane was sandwiched between them and supported on a Teflon support screen. The membrane holder had three openings: the first was a feed entrance and the second was for N₂ feeding, both on the top cover, while the third was located at the bottom, and was used for product collection. A stainless steel (316 L) vessel was used as a surge tank for regenerating solution (1N H₂SO₄).

Testing and Evaluation of the Integrated Unit to Produce Biofuel/Biodiesel

Two experiments were performed using the developed pilot unit. The first esterification reaction was carried out to produce ethyl acetate at operating conditions of molar ratio 2:1 ethanol to acetic acid at 25°C under 2 bar nitrogen pressure for 60 min then shifted to the other reactor, while the first one was subjected to the regeneration step using 1N H₂SO₄ at 25°C under

the same nitrogen pressure for 20 min; subsequently the esterification reaction returned to the regenerated membrane in the first reactor, while the other membrane in the second reactor was exposed to the regeneration step. This trend was repeated alternately for 6 hours. The second esterification reaction was carried out to produce fatty ester using fatty acid (ethyl hexanoic acid) with ethanol. It was conducted using the same procedures and conditions except that the reaction was performed at molar ratio 5:1 ethanol to fatty acid. The samples were collected and analysed by gas chromatography.

The reaction conversion was calculated based on the change in the concentration of acetic acid or fatty acid in the product compared by the feed using the following equation:

$$\text{Conversion \%} = 100 * \frac{C_f - C_p}{C_f}$$

where C_f is the concentration of acid in the feed and C_p is the concentration of acid in the product.

RESULTS AND DISCUSSION

Membrane Preparation, Grafting and Characterisation

Asymmetric flat sheet polyethersulfone (PES) membranes were prepared by the phase-inversion method; the prepared membrane before and after grafting is illustrated in Fig.5. The grafting process of the prepared membrane was carried out using one reactor of the developed unit, passing a solution of 1N H₂SO₄ at temperature 60°C for 1 hr at the initiation step and 12% styrene at 25°C for 10 min in the polymerisation step and finally 1N H₂SO₄ at 25°C for 1 hr in the termination step of the grafting process. A scanning electron micrograph was used to assess the grafted membrane surface; Fig.6 indicates that the grafted membrane pores were wider than the original one and seemed lesser in number (El-Zanati *et al.*, 2011, Abdallah *et al.*, 2013).

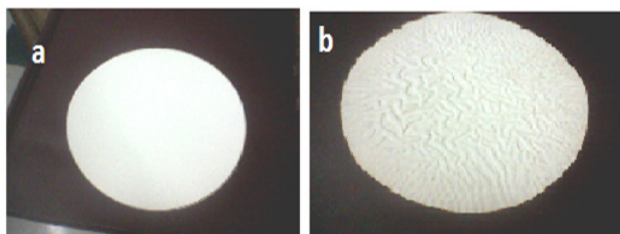


Fig.5: Prepared membrane (a) before grafting and (b) after grafting.

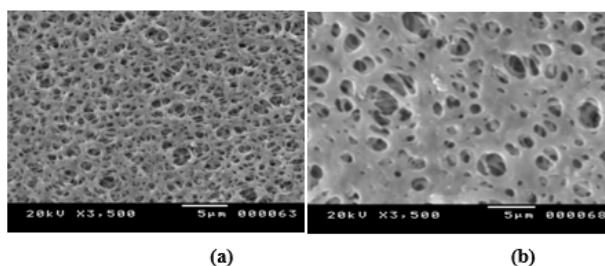


Fig.6: SEM picture of grafted membrane surface, the magnification power was 10 kv.

Integrated of Esterification/Regeneration Processes Set-Up

The integrated reaction/regeneration unit is captured in Fig.7. The unit was used in an NRC workshop. It operates as described earlier; each reactor is fed with reactants from a surge vessel of capacity sufficient for a running time of 1 hr and provided with an adjustable valve to control the flow rate. Also, each reactor was connected with a tank of diluted sulphuric acid of a capacity sufficient for running 20 min for regeneration. The product is collected continuously from each reactor and collected in a holding tank. An example of the scheme using two consecutive cycles, comprising all equipment and operating time, follows this process: the filling of tanks, reaction and regeneration steps etc. Table 1 illustrates the GANTT chart and schedule of working time i.e. 210 min.

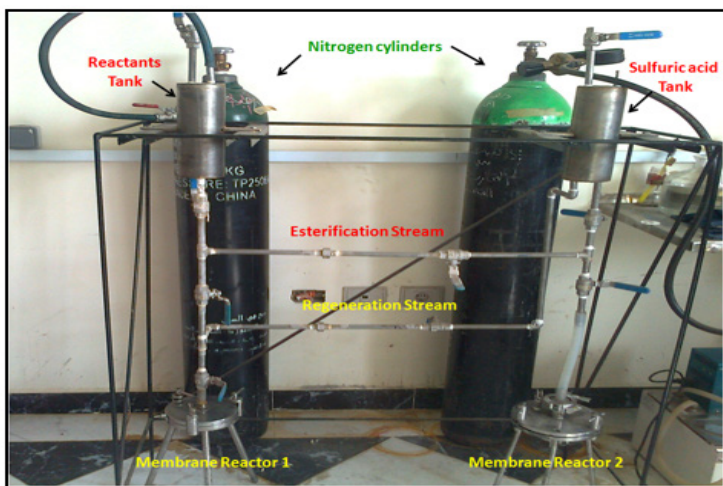


Fig.7: Pilot integrated unit for reaction and regeneration.

TABLE 1 : GANTT Chart and Schedule Working Time for Two Cycles (210 min)

Process/task	Time*10 (min)																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Filling of reactant feeding vessel	█																				
Filling of regeneration solution feeding vessel		█																			
Feeding R1 with reactants			█	█	█	█	█	█	█												
Esterification reaction in R1				█	█	█	█	█	█												
Feeding regeneration solution to R1										█	█										
Regeneration of membrane of R1											█	█									
Feeding R2 with reactants													█	█	█	█					
Esterification reaction in R2														█	█	█	█				
Feeding regeneration solution to R2																					
Regeneration of membrane of R2																					
Feeding R1 with reactants																					
Esterification reaction in R1																					
Feeding regeneration solution to R1																					
Regeneration of membrane of R1																					
Feeding R2 with reactants																					
Esterification reaction in R2																					

Testing and Evaluation by Flow-Through Esterification Reaction

The esterification reaction using a catalytic membrane at 2:1 ethanol to acetic acid, at room temperature and under 2 bar nitrogen pressure was conducted. The change of reaction conversion with time is illustrated in Fig.8. The results indicated a maximum peak at the beginning of the reaction, where the conversion reached about 96% after 10 sec of reaction time. During the process the conversion decreased until it reached 93% after 60 min; at this point the regeneration step was started and the other membrane holder was used to continue the reaction. This was repeated for six hours.

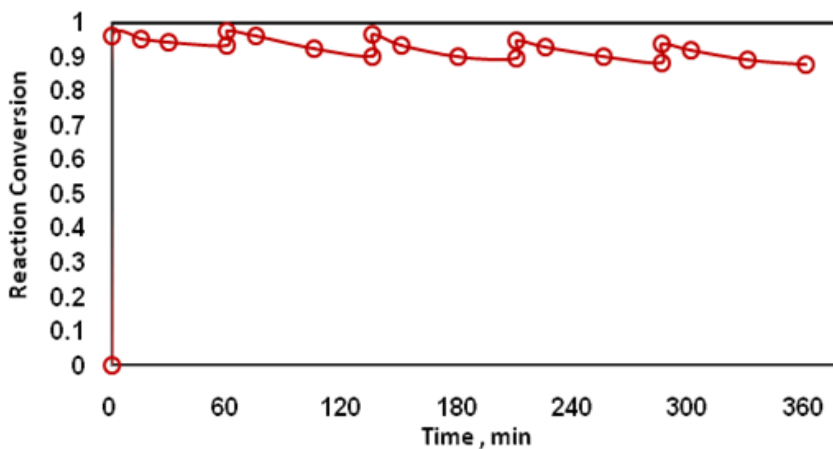


Fig.8: Flow-through esterification process with catalytic membrane using 2:1 ethanol to acetic acid.

The experiments were repeated to produce fatty ester. Fig.9 illustrates the flow-through esterification reaction by catalytic membrane using 5:1 ethanol to fatty acid (ethylhexanoic acid). The maximum peak conversion reached 97.7 % at the beginning of the reaction and decreased during the reaction time to minimum peak conversion at 92% after 60 min. This was repeated for six hours.

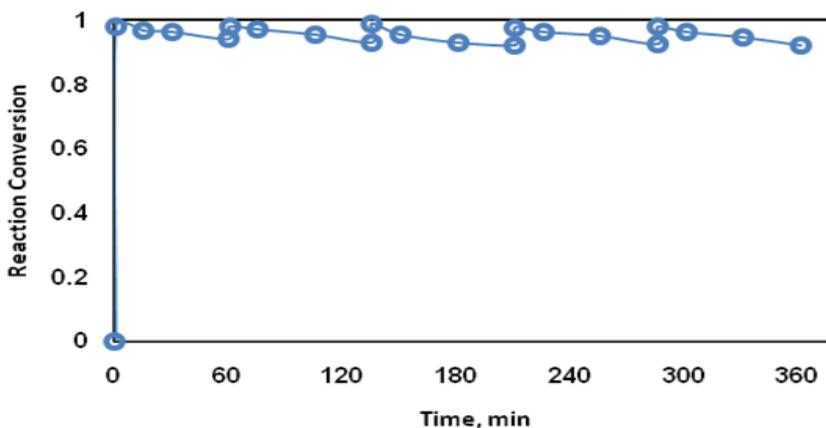


Fig.9: Flow-through esterification process with catalytic membrane using 5:1 ethanol to fatty acid.

The experiment succeeded in obtaining almost constant reaction conversion for both investigated reactions to assess and evaluate the designed unit where the average reaction conversion was 96-98%. However, this process increased productivity in a short time and decreased the separation cost (Abdallah *et al.*, 2013).

CONCLUSION

The functionalised catalytic membrane of sulfonated polystyrene grafts acts as an alternative to the conventional esterification process. An integrated pilot unit was developed to produce esters continuously; it comprised two units working simultaneously at two steps i.e. the reaction and regeneration steps. The first reactor operated for a period of 60 minutes before the reactant flow was shifted to the second reactor. The first reactor was then subjected to dewatering and membrane regeneration for 20 minutes. The integrated pilot unit afforded a high esterification comprehensive reaction conversion of 96-98% for esterification of acetic acid and fatty acid with ethanol, respectively.

REFERENCES

- Abdallah, H., Said, F., Ahmed, E., El-Arady, O., & El-Zanati, E. (2013). Development and preparation of microfiltration polyethersulfone membrane for catalytic membrane application. *Journal of Applied Sciences Research*, 9, 1623-1634.
- Abdallah, H., El-Gendi, A., El-Zanati, E., & Matsuura, T. (2013). Pervaporation of methanol from methylacetate mixture using polyamide-6 membrane. *Desalination and Water Treatment*, 51(40-42), 7807-7814.
- Buonomenna, M., G., Choi, S., H., & Drioli, E. (2010). Catalysis in polymeric membrane reactors: The membrane role. *Asia-Pacific Journal of Chemical Engineering*, 5(1), 26-34.
- El-Zanati, E., Ritchie, S., Abdallah, H., Ettouny, R., & El-Rifai, M. (2011). Esterification catalysis through functionalized membranes. *International Journal of Chemical Reactor Engineering*, 9(1), 1542-6580.
- El-Zanati, E., & Abdallah, H. (2012). Development of functionalized catalytic membrane for ethyl ester production. *International Journal of Emerging Trends in Engineering and Development*, 5, 505-521.
- El-Zanati, E., Ritchie, S.M.C., Abdallah, H., & Elnashaie, S. (2014). Mathematical modeling, verification and optimization for catalytic membrane esterification micro-reactor. *International Journal of Chemical Reactor Engineering*, 13(1), 71-82.
- Maria, T., Sanza, J., & Urgan, G. (2006). Esterification of acetic acid with isopropanol coupled with pervaporation Part II. Study of a pervaporation reactor. *Chemical Engineering Journal*, 123(1), 9-14.
- Mbaraka, I. K., Radu, D. R., Lin, V. S. Y., & Shanks, B. H. (2003). Organosulfonic acid functionalized mesoporous silicates for the esterification of fatty acid. *Journal of Catalysis*, 219(2), 329-336.
- Ozdemir, S. S., Buonomenna, M. G., & Drioli, E. (2006). Catalytic polymeric membranes: Preparation and application. *Applied Catalysis A: General*, 307(2), 167-183.
- Sawant, D. P., Vinub, A., Justus, J., Srinivasu, P., & Halligudi, S. B. (2007). Catalytic performances of silicotungstic acid/zirconia supported SBA-15 in an esterification of benzyl alcohol with acetic acid. *Journal of Molecular Catalysis A: Chemical*, 276(1), 150-157.

- Shah, T. N., & Ritchie, S. M. C. (2005). Esterification catalysis using functionalized membranes. *Applied Catalysis A: General*, 296(1), 12-20.
- Shah, T. N., Goodwin, J. C., & Ritchie, S. M. C. (2005). Development and characterization of a microfiltration membrane catalyst containing sulfonated polystyrene grafts. *Journal of Membrane Science*, 251(1), 81-89.
- Shi, W., He, B., Cao, X., Li, J., Yan, F., Cui, Z., Zou, Z., Guo, S., & Qian, X. (2013). Continuous esterification to produce biodiesel by SPES/PES/NWF composite catalytic membrane in flow-through membrane reactor: Experimental and kinetic studies. *Bioresource Technology*, 129, 100-107.
- Westermann, T., & Melin T. (2009). Flow-through catalytic membrane reactors: Principles and applications. *Chemical Engineering Processing*, 48(1), 17-28.
- Westermann, T., Kretzschmar, E., Pitsch, F., & Melin, T. (2009). Heat transfer and temperature profiles in flow-through catalytic membrane reactors, *Chemical Engineering Journal*, 155(1), 371-379.