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Applicability of membrane reactor for producing environment friendly fuel additive glycerol carbonate

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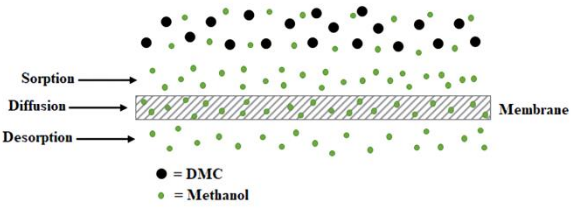
Graphical abstract



Sorption Diffusion Mechanism

Abstract

Production of glycerol carbonate (GLC) that is a fuel additive from green solvent dimethyl carbonate (DMC) and biodiesel by-product glycerin is environmentally friendly synthesis. The usage of waste glycerol from biodiesel plant makes the production cost lower. When the membrane aided technique is used for the production of GLC, this technique will be very promising technique. Because membrane applications are environment and energy friendly economical applications. The production with membrane aided can be made by catalytic membrane. In this study, catalytic membranes were developed from synthetic and natural materials to produce GLC by transesterification reaction between glycerol and DMC. The reaction gives methanol as byproduct. The catalytic membranes were used methanol retentive material for increasing the reaction conversion of glycerol to glycerol carbonate. The synthetic catalytic membrane materials were poly(vinylalcohol)(PVA), poly(vinylpyrrolidone) (PVP), Poly(4-vinylpyridine) (P4VP) polymers and CaO. The natural catalytic membrane material was chitosan biopolymer and waste eggshell. The properties of by-product methanol retentive of the polymeric membranes were determined from sorption tests. The tests were shown that the catalytic membranes would sorp by-product methanol during reaction. This pointed out that GLC synthesis can be made by membrane aided technique such as membrane reactor.

Keywords: Glycerin carbonate, fuel bioadditive, catalytic membrane.

1. Introduction

Today the development of the industry, increasing energy demand and diminishing fossil fuels are increasing the demand for new and renewable fuels. Biofuels that can meet the energy need to a large extent; being environmentally friendly, low in gas emissions and ease of recycling are interesting in this concept.

The growing demand for biofuels also highlighted biodiesel production and revealed glycerine as a by-product in high quantities at low prices and in this context, laboratory-scale studies on the effective evaluation of glycerine are ongoing (Bher *et al.*, 2008; Ishak *et al.*, 2017; Kerton *et al.*, 2009; Ochoa-Gómez *et al.*, 2012; Teng *et al.*, 2014).

Glycerine; 1,2,3-Propantriol is the common name. This colorless liquid with syrup consistency is soluble in water. It is included in animal and vegetable fat substances. When applied to the skin, it is added to the structure of lipids (fats). It is used as a softener in medicine and in the production of soap and special fabrics in industry. Glycerine obtained by saponification of oily substances is a trihydric alcohol; that is, it contains three hydroxyl groups (OH), each connected to a different carbon atom. Other uses of glycerine include the production of industrial solvents. Glycerine also helps to reduce the water activity value in foods.

Glycerine carbonate is one of the glycerine derivations which are used in chemical industry by productions. Generally, it is used as a protic solvent in resin plastics, adhesive additive, surface activator, ink, paint industry and lubricant. In addition to this, glycerin carbonate formed by reaction of dimethyl carbonate and glycerin is also used as biofuel additive. Compared to the production methods commonly encountered in the literature the chemicals (glycerine and dimethyl carbonate) used in this process are non-toxic and are primarily preferred for their compliance with environmental and green chemistry principles (Lingaiah *et al.*, 2011).

Glycerin carbonate (GLC), known by its chemical name 4-hydroxymethyl-1,3-dioxolan-2-one, stands out for its physical and chemical properties. The chemical reaction of

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glycerin carbonate formation is shown in the Figure 1 (Bher *et al.*, 2008; Kerton *et al.*, 2009; Teng *et al.*, 2014).

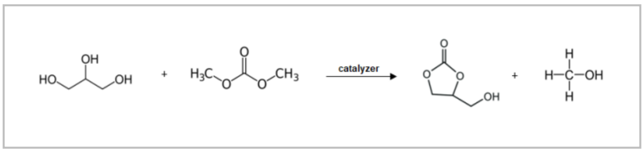


Figure 1. Chemical reaction of glycerol carbonate with glycerol and DMC

Glycerine carbonate (GC) is a not flammable, nontoxic, biodegradable, water-soluble, and viscous with a very low evaporation rate and moderate properties of glycerin carbonate increase usability.

The uses of glycerin carbonate are summarized as follows: Chemical agent, Cosmetic, Medical, Pharmaceutical Industry, Lithium Batteries, Cleaning Agent, Bioadditive fuel.

Some studies in the literature are as follows also:

Lingaiah *et al.* Performed glycerine carbonate with DMC and glycerol in the presence of trimethalic catalyst. They concluded that trimetallic catalysts were more active than bimetallic catalysts (Lingaiah *et al.*, 2011).

Simanjuntaka *et al.* Performed CaO catalyzed transesterification of DMC with glycerol in the presence of isolated CaO catalyst and produced glycerine carbonate in 90% yield (Simanjuntaka *et al.*, 2011).

Liua *et al.* LDOx for transesterification reaction between dmc and glycerine to glycerine carbonate, by calcined mixed oxides (Liua *et al.*, 2013).

Roschata *et al.* studied the CaO catalyst for the transesterification of glycerine carbonate with a molar ratio of dimethyl carbonate and glycerol of 3: 1 and a catalyst loading of 3% at 80° C. CaO was obtained economically by calcining eggshells, golden apple snail shells and cockle shells. All CaO catalysts obtained by calcination within 2 hours they observed that they showed very high catalytic activity in this reaction by providing glycerol carbonate yield of over 92.1% and concluded that the shells used as catalysts were not only green and inexpensive but also had high potential for high yields of glycerol carbonate product.

In this study, polyvinyl alcohol (PVA) polymer was used due to hydrophilic property PVP membrane has been selected to use methanol selective property and P4VP membrane as basic catalyst (Albadi *et al.*, 2013; Bessbousse *et al.*, 2009; Chen *et al.*, 2016; Dmitrenko *et al.*, 2018; Jagtap *et al.*, 2007; Kang *et al.*, 2010; Liu *et al.*, 2019; Lu *et al.*, 2003; Park *et al.*, 2018; Rosli *et al.*, 2018; Shankhwar *et al.*, 2015; Zhu *et al.*, 2013). Polymeric membrane blends were prepared firstly. Then, synthetic based catalytic membranes were made by adding CaO to these membranes and used in GLC synthesis.

Chitosan polymer was choseed because of its biodegradability and high hydrophilic activity; egg shell was chosen for its catalytic activity feature. Chitosan that is produced from sea shells has also hydrophilic properties and biodegrability and it is an environmentally friendly natural biopolymer (Antony *et al.*, 2019; Gaoa *et al.*, 2012; Ochoa-Go´mez *et al.*, 2009; Pandit *et al.*, 2017). Eggshell was chosen because of catalytic activity and low cost. It is a green and economic catalyst material (Antony *et al.*, 2019; Roschata *et al.*, 2018; Yasmeen *et al.*, 2015).

PVA, PVP, PV4P and CaO were used as synthetic materials to make catalytic membranes to synthesis of GLC. Chitosan and egg sheel were used as natural materials to make catalytic membrane to synthesis of GLC.

GLC is produced from glycerol and DMC, methanol is formed by-product. To improve conversion of glycerol to GLC excess reactant is used or by-product is removed. Removing of a byproduct by catalytic membrane is an innovative way in the reactions.

In a reaction limited by thermodynamic equilibrium, the presence of a membrane makes it possible to overcome the limitations of conversion in the conventional reactors, which is limited by thermodynamic equilibrium. This is because, according to the Le Chatelier's principle of the membrane cell used in the process; in the relevant reactions; It is the selective removal of a product by acting as a slip effect on the membrane cell, and thus the respective reaction becomes a progressive process with a higher yield (Amiri *et al.*, 2020; Bagnato *et al.*, 2017; Iulianelli *et al.*, 2018; Plazaola *et al.*, 2017). Removing of a byproduct during the reaction is generally to increase the reaction efficiency by changing the thermodynamic equilibrium consistent with the principle. Besides that, another functionality of membrane reactors is represented by the control of the addition of reactants to increase the overall reaction conversion by eliminating the disadvantages of secondary reactions, and to shift the equilibrium transformation towards products by creating more domains on the membrane surface (Dittmeyer *et al.*, 2017; Karakhim *et al.*, 2020; Lee *et al.*, 2019; Lee *et al.*, 2020; Plazaola *et al.*, 2017; Pramanik *et al.*, 2019).

In the membrane reactor applications by-product is transported from the reactor and thus the conversion is increased.

Membrane reactors (MR) were discovered in the mid-19th century, the development of membrane reactors; it has increased with the development of new membranes and the importance of temperature parameter in processes (Amiri *et al.*, 2020). Membrane reactor (MR) technology plays an important role in the process, as it is a highly advantageous process for performing both the chemical reaction and the separation process simultaneously. Thus, facilities using membrane reactors become more compact with lower investment costs and cost-effective process (Bagnato *et al.*, 2017)

Pervaporation process: it is a membrane process in which liquid-liquid mixtures can be separated under vacuum with high selectivity. Depending on the working principle, it is accepted as one of the efficient and sustainable technologies that can replace traditional separation processes with its ability to be carried out at low temperature and pressure. The basis of the pervaporation process; by using an active or passive membrane in the system; it is based on the separation of a mixture by its passage from one site to another, based on the sorption diffusion mechanism. The sorption diffusion mechanism is given in Figure 2. According to the sorption diffusion mechanism, it is predicted that the DMC-Methanol mixture would separate as seen in Figure 2.

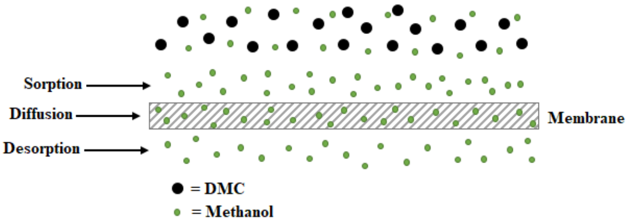


Figure 2. Sorption diffusion mechanism

Here the driving force is the chemical potential difference corresponding to the concentration gradient in the reaction. In this process where the pervaporation process creates a hybrid with the membrane; it is also called pervaporation membrane reactor. Transport event through integrated membrane at PVMR system; dissolution is explained by the diffusion mechanism. When the liquid reactants fed to the system come into contact with the membrane surface, a driving force is created with the help of the vacuum pump and thus, one component transports through the membrane. The component absorbed by the membrane diffuses across the surface of the membrane. Then the absorbed component is removed from the system by desorption in the vapor phase from the vacuum applied side of the membrane. With the component removed from the system in vapor phase under continuous vacuum, the reaction conversion is increased by shifting the equilibrium in the direction of the products (Abdallah *et al.*, 2013; Chandane *et al.*, 2016; Jyoti *et al.*, 2017; Qing *et al.*, 2017a, 2017b; Shuita *et al.*, 2019; Unlu *et al.*, 2018; Xue *et al.*, 2019). When pervaporation (PV) is used membrane process membrane reactor is defined as pervaporation membrane reactor (PVMR).

Chemical reactions and separation/purification processes play a key role in the chemical industry. However, most conventional industrial separation processes such as distillation cause a lot of energy consumption and therefore high costs. Therefore, it has become important to improve chemical reactions and subsequent separation processes for an efficient and effective process. Membrane separation processes are a separation technique that can be performed efficiently on a large scale and is an alternative to conventional separation processes in terms of both energy and total cost. Generally, catalytic reactions have become the focus of researchers in science and engineering, with both the realization of the reaction and the simultaneous separation of the desired products. The membrane-based combination of catalytic reactions and separation processes is the main element behind catalytic membrane reactors (CMRs). The most obvious advantages of CMRs are that they are very functional in the reactor by selectively removing a product, containing solid or liquid phase catalysts on its surface or in it, or in some cases acting as a direct catalyst. Catalytic membrane reactors also; It complies with green and sustainable chemical and chemical engineering principles with its lower energy requirement, lower pollution feature and effective-efficient system performance (Hafeez *et al.*, 2020; Murmura *et al.*, 2017; Zhang *et al.*, 2018).

If a catalytic membrane is used pervaporation membrane reactor is defined as pervaporation catalytic membrane reactor (PVCMR).

In this study, it was aimed to investigate applicability of PVCMR in the production of GLC. For this purpose, the catalytic membranes were developed for using at the reaction.

In order to investigate pervaporation properties sorption tests were made for methanol. Swelling values were obtained from sorption results. Sorption ability of a membrane indicates diffusion ability from the membrane. Prefential sorption of a component to a membrane causes prefential permeation of the component through the membrane. Because sorped component in the membrane permeates from the membrane, this situation gives an idea about the membrane reactor application. When byproduct of transesterification reaction removes from the reactor by the membrane conversion increases. Thus, the conversion can increase by application of the membrane reactor. Interaction between the membrane and components is defined by sorption tests. The membrane that sorps byproduct is used in the membrane reactor. In this study byproduct methanol sorption tests were made by using the prepared membranes. Pervaporation properties of all membranes were defined by sorption tests for methanol.

2. Materials and methods

2.1. Chemicals

Poly(vinyl alcohol) (PVA) (Mw ~ 125,000kg/mol), Chitosan polymer(in powder form), Poly(vinylpyrrolidone)(PVP) and Poly(4-vinylpyridine)(P4VP) had been bought from Sigma Aldrich; dimethyl carbonate(DMC), glycerin; calcium oxide(CaO) and acetic acid from Merck. Additionally, egg shells as catalysts were used from kitchen waste.

2.2. Catalytic membrane preparation method

Catalytic membranes had been provided for by solution pouring and evaporation technique. Wt.% 10 of PVA and PVP wt.% 5 were dissolved in deionised water at 90°C temperature for three hours. P4VP wt.%5 was dissolved in wt.%2 acetic acid solution at 50°C temperature for two hours. Thereafter, the epichlorohydrin cross-linking agent was added to the prepared polymer solution as 0.1% by weight and it was stirred at room conditions for 24 hours. Homogenization of the polymeric solution, catalyst added the polymer solution was poured into polymetacrylate surface, annealed at 50°C for 48 h.

Catalytic membrane solutions were prepared by adding catalyst CaO to the solutions of pristine polymeric membranes. After that the solutions were poured and dried. Thus, catalytic membranes as heterogeneous catalysts were formed.

CaO was added to support Glycerin Carbonate (GLC) synthesis and to give extra catalytic properties to the system.

Biodegradable catalytic membranes had been prepared by solution pouring and evaporation tecnique. Chitosan at 1% by weight was dissolved in 1% by weight acetic acid solution at 40°C for 12 hours. Then, 0.05% by weight epichlorohydrin crosslinking agent put in polymer solution after that merged at room temperature during 24 hours to ensure homogenization. Egg shells were obtained naturally and washed with distilled water for sterilization in the laboratory and powdered with a disintegrant and dried at 100°C for 2 hours, then calcined at 1000°C for 2 hours to ensure catalytic activity. After the calcination process, the polymeric solution prepared and the egg shell activated that it is 3% by weight of the polymer amount in the solution was added gradually and mixed until a homogeneous solution was obtained. The solution prepared in this way was pouring into a polymetacrylate surface and dried 40°C during 12 h.

2.3. *Membrane and catalyst characterization*

Cross-linking reaction within the active groups in membrane and the catalyst active group were examined by ftir instrument. The catalytic distribution of the catalyst in the catalytic membrane was examined by a polarized optical microscope (POM) using nikon eclıpse LV100POL. Thermogravimetric Analysis (TGA) of catalytic membrane was examined by using Mettler Toledo.

2.4. *Glycerine carbonate synthesis*

GLC had been formed at 70 ºC and 3% catalyst loading with molar feed ratios of 3:1. The reaction system is supported with a reflux unit to keep the reaction conditions stable and any reactant losses that may occur. By-product methanol, residual DMC formed during glycerin carbonate synthesis reaction were removed from the system by evaporation.

2.5. *Glycerine carbonate analysis*

There are different methods for the determination of glycerin carbonate in the literature. The most common of these are the determination of glycerin carbonate by gas chromatography and by FTIR analysis. In this study, glycerin carbonate was analyzed by FTIR method.

The determination of glycerin carbonate by FTIR is carried out as follows: Calibration curve is generated by FTIR analysis with glycerine-glycerine carbonate solutions prepared at different concentrations to determine glycerine carbonate conversion. In the literature, glycerin carbonate peaks were found between 1785 cm-1 and 923 cm-1. The ratio of these peaks to each other gives the glycerin carbonate amount. Glycerine conversion can be calculated with the help of empirical equation 1 and calibration curve (Ochoa-Go´mez *et al.*, 2009):

$$C = \frac{100.M_{OG} - M.X_G}{M_{OG}} \qquad (1)$$

X_G given in Equation 1 is the amount of glycerin in the reaction; M is the residual reactant amount at the end of the reaction and M_{OG} is the total initial mass of glycerin.

3. Results and discussion

3.1. *Membrane characterization*

PVA+CaO catalytic membrane was selected for investigation of characterization. It was quessed from pretesting that PVA+CaO catalytic membrane would be the proper membrane for the GLC synthesis. For the purpose of determine the effect of CaO incorporation to the membrane, characterization tests were performed. In the catalytic membrane CaO was used to provide catalytic property to the PVA membrane. FTIR spectra of the pure (non-crosslinked) and CaO containing membranes were shown in Figure 3.

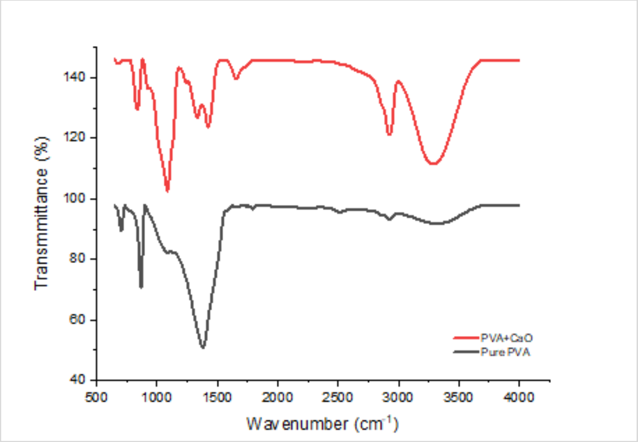


Figure 3. FT-IR Spectroscopy analysis for pure PVA and PVA with Cao

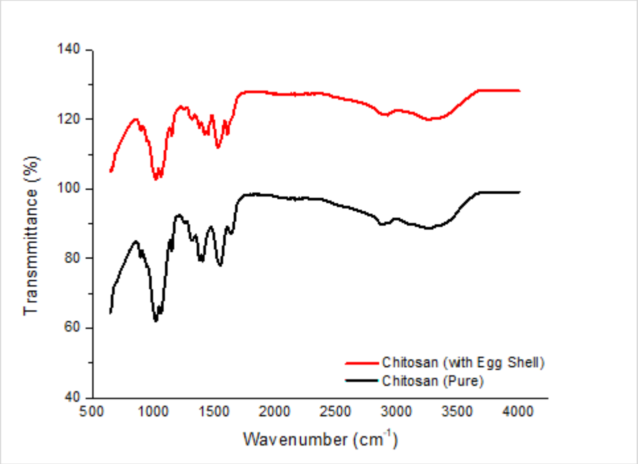


Figure 4. FT-IR spectroscopy analysis for pure chitosan and chitosan with egg shell

In the pure and catalytic membrane, epichlorohydrine was used as crosslinking agent to restrain solvation of membrane within the aqueous media and the reduction in OH peak after crosslinking reaction be aimed in membranes. FTIR spectra of the pure and with CaO containing membranes were given in Figure 3. As it could be seen in Figure 3, characteristic peak of -OH bond was seen in the 3272 cm^{-1} region and the intense of the peak significantly reduced by incorporation of epichlorohydrine. Characteristic peaks were seen in the between 883 cm^{-1} and 1449 cm^{-1} (Pandit *et al.*, 2017).

FTIR analysis results of pure chitosan and chitosan with egg shell were given in Figure 4. Characteristic functional groups of chitosan in FTIR analysis were between at 500-4000 cm^{-1} as seen in the literature. The peak N-H indicating the characteristic amine group of chitosan was found at 1570 cm^{-1}, while -OH group was examined at 3475 cm^{-1}, C-H group at 2925 cm^{-1} (Yasmeen *et al.*, 2015).

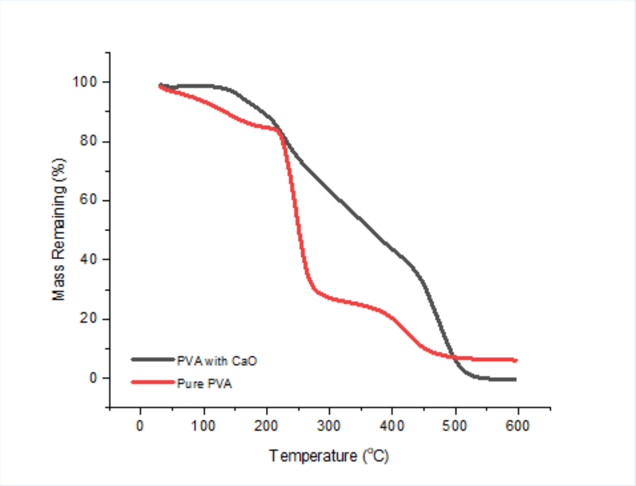


Figure 5. TGA analysis for pure PVA and PVA with CaO

PVA pure membrane and PVA-CaO catalytic membrane were examined by thermal gravimetric analysis. In Figure 5, TGA result of pure PVA shows the percentage degradation of pure PVA precursors heated between 25 ºC-600 ºC in a controlled conditions with a certain temperature rise. It has been understood that there is no degradations at the synthesis conditions. Moreover, in order to explain the effect CaO, it is investigated PVA-CaO catalytic membrane with thermal gravimetric analysis showed Figure 5.

TGA analysis results of pure PVA membrane and CaO added PVA catalytic membrane are compared; It has been interpreted as that CaO changes the mechanical properties of the PVA polymer and also reduces the degradation time.

TGA analysis of chitosan pristine membrane, chitosan catalytic membrane were given in Figure 6. TGA analysis carried out at 25°C-600°C. Mass losses for chitosan pristine membrane are important later from 270°C, the increment in bulk loss after 270 ° C is seen in an increasing direction and more rapidly. It is consequence that these degradation rates will not negative impact on the reaction when the reaction conditions were considered. Additionally, in the hybrid membrane prepared by adding egg shell into chitosan; It has been shown that the strength of the membrane is increased by TGA characterization. The reason of this is the eggshell obtained by natural ways contains a high amount of CaO. In the previous study (Yuzer N.Y. and Hilmioglu N. 2019a, Yuzer N.Y. and Hilmioglu N. 2019b) as a result of the analysis of CaO loaded on the catalytic membrane, it was found that CaO directly affect the strength of the membrane.

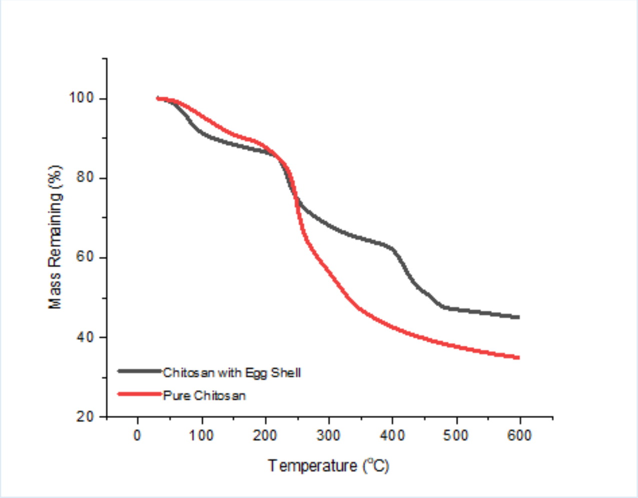


Figure 6. TGA analysis for pure chitosan and chitosan with egg shell

From the analysis of CaO and eggshell loaded polymeric membranes, it was found that CaO and eggshell directly affect the strength of the catalytic membranes (Gaoa *et al.*, 2012).

As a result, it was confirmed that the CaO and eggshell catalyst used for both hybrid catalytic membranes (PVA-CaO and Chitosan-Eggshell) have a strength-enhancing effect and would not cause decomposition by temperature during the reaction.

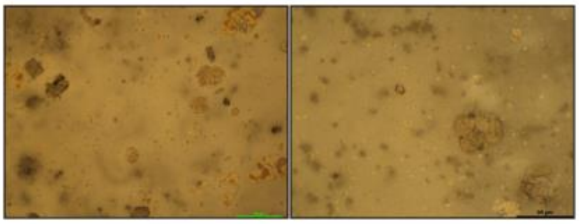

(a) 20x Free CaO (b) 50x Free CaO

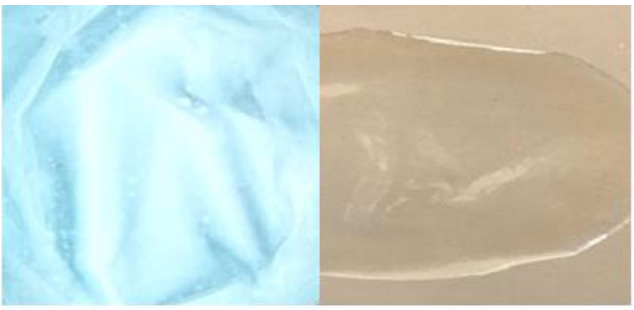
Figure 7. Polarized Electron Microscope (POM) Images of CaO; (a)20x Free CaO (b) 50x Free CaO

The crystal structure of CaO catalyst examined by polarized optical microscope in shown Figure 7. It showed that CaO was stable as catalyst. It is understood that the free catalyst is suitable for catalytic membrane application (PVA+CaO).

Images of pristine PVA and catalytic CaO loaded PVA membranes were given in Figure 8.

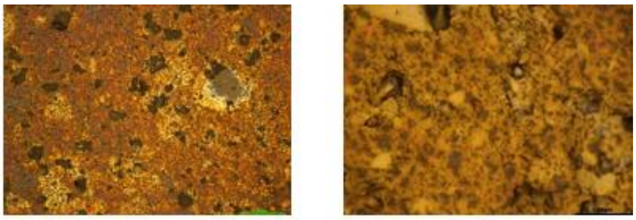
Configuration of the free CaO was stable and the adaptation of it with the polymeric membrane solution was evaluated for stabilization showed in Figure 8a and 8b.

In Figure 9, the crystal structure of the eggshell catalyst, which was obtained from domestic wastes and provided catalytic activity after calcination, was examined by polarized electron microscope (POM). The crystal configuration of egg shell was given in Figure 9. It showed that egg shell was stable as catalyst. Egg shell as free catalyst is suitable for catalytic membrane application (Chitosan+egg shell).



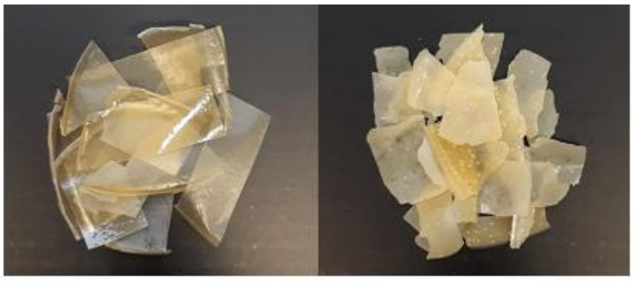
(a) (b)

Figüre 8. PVA Membrane images; (a) CaO loaded PVA catalytic membrane;(b) Pure PVA membrane



(a) (b)

Figure 9. Polarized electron microscope (POM) images of eggshell; (a)20× free eggshell (b) 50× free eggshell



(a) (b)

Figure 10. Chitosan membrane images; (a) Pure chitosan membrane; (b) Catalytic chitosan membrane

The images of pristine chitosan membrane and egg shell loaded chitosan membrane were given in Figure 10. As shown in Figure 10 a and b, it was observed that the configuration of the free catalyst was steady state and the adaptation of the catalyst with the membrane solution was evaluated for stabilization.

3.2. Swelling tests

Degrees of swelling were estimated using the following Equation 2

$$DS(\%) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (2)$$

W_1=Dry catalytic membrane weight

W_2=Wet catalytic membrane weight

Chitosan, PVA and PVA-PVP membrane film pieces were kept in pure solvents for 24 hours and were subjected to sorption tests to determine the equilibrium period. Figure 11 shows the degree of swelling of the membrane films. Due to the strong hydrophilic structures of chitosan, PVA and PVA-PVP membranes, it is expected that the by-product methanol formed as a result of glycerin carbonate synthesis will be absorbed and thus the reaction will shift towards the products. While chitosan, PVA and PVA-PVP based membranes have high methanol selectivity; Chitosan and PVA membranes have no DMC and glycerin selectivity, whereas PVA-PVP membrane has sorped DMC for a small value that can be eliminated. As a result of these data, it is concluded that chitosan, PVA and PVA-PVP membranes can be used in the system in the glycerin carbonate synthesis reaction, reaction can continue towards to products and therefore the reaction conversion values increase.

Although PVA and PVP had hydrophilic property PVA/PVP based membrane sorped byproduct methanol together with DMC while the membrane did not sorp glycerin.

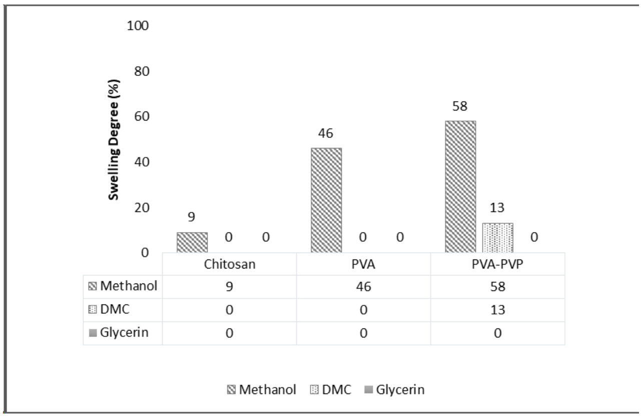


Figure 11. Swelling degrees of the different hybrid membranes

3.3. Reaction results

GLC (glycerine carbonate) synthesis was executed with different catalytic membranes prepared and glycerine carbonate conversion was shown in Figure 12.

The glycerin carbonate was synthesized at the batch reactor with a reflux by the help of different catalytic membranes prepared. The highest reaction conversion value was obtained with eggshell loaded chitosan membrane. Pieces of eggshell loaded chitosan membrane added to the reactor increased the reaction conversion by absorption of by-product methanol by chitosan while egg shell catalyzed the reaction.

Calculating the conversion of glycerin in the reaction; it is done by using a simple equation (equation 1) with the value read from the calibration curve (Ochoa-Gómez *et al.*, 2009).

Pristine PV4P basic polymeric membrane gives 35 wt% GLC conversion value alone. This situation was proved the catalytic property of PV4P.

44 wt% GLC conversion was obtained by PVA+PVP+PV4P+CaO catalytic membrane. PV4P and CaO gave catalytic effect, PVA and PVP sorped by-product methanol in the PVA+PVP+PV4P+CaO catalytic membrane.

PVA+CaO catalytic membrane had sorption and catalytic effects respectively by giving 45 wt% GLC conversion.

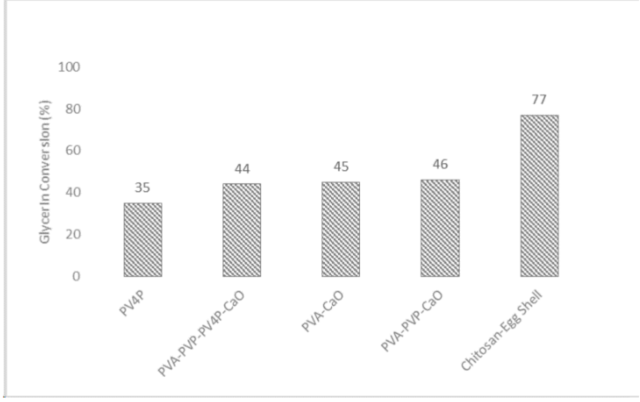


Figure 12. Glycerin carbonate reactions data with different catalytic membranes (reaction conditions; *M*=3:1 (DMC:Glycerin); *T*=70°C; catalyst loading 3%)

In the PVA+PVP+CaO catalytic membrane CaO had catalyst function PVA and PVP had separator function. 46 wt% GLC conversion was shown by PVA+PVP+CaO catalytic membrane.

In order to enhance the catalytic activity, catalytic membranes were made by adding catalyst to hybrid blend membrane. Experimental studies showed that the best conversion value was in PVA+PVP+CaO catalytic membrane. PVA+CaO catalytic membrane had approximate conversion value with PVA+PVP+CaO. Therefore PVA loaded CaO catalytic membrane made from synthetic materials can be used for the GLC synthesis.

Chitosan loaded eggshell catalytic membrane made from natural materials showed highest conversion value for the GLC synthesis. The success of this membrane was related to its sorption ability of only byproduct methanol.

The conversion results of glycerol to GLC showed that chitosan loaded eggshell membrane as natural based catalytic membrane has higher conversion value than the other synthetic based catalytic membranes. The reason for this was chitosan loaded eggshell catalytic membrane sorped only byproduct methanol not sorped reactant DMC. Retention of methanol by chitosan catalytic membrane increased the conversion. PVA/PVP loaded CaO membrane had reasonable conversion value and highest swelling degrees. However PVA/PVP loaded CaO catalytic membrane sorped methanol with DMC together. Retention of byproduct and reactant together by PVA/PVP catalytic membrane decreased the conversion. In our trial test study, it was shown that chitosan/PVA blended membrane had higher swelling degree for methanol than pure chitosan membrane and no swelling degree for DMC. This membrane can be another alternative membrane material for making a new catalytic membrane for obtaining higher conversion values also.

4. Conclusion

Transesterification reactions are limited by thermodynamic equilibrium. Addition of catalyst to the system alone is not sufficient to increase the reaction conversion, as well as removal of the by-product methanol comprised at the finally of the reaction from the system plays an effective role in increasing the reaction conversion. The studied catalytic membranes have synergic property in this respect.

The prepared catalytic membranes catalyzed the reaction and sorped by product. The catalytic membranes have potentials for energy and environment friendly synthesis of GLC economically. It was concluded that membrane reactor specially pervaporation catalytic membrane reactor can be applicable for glycerol carbonate synthesis. In the practical application of PVCMR, the catalytic membranes both could catalyze reaction and separate byproduct for obtaining higher conversions.

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