

Progress on Zeolite-membrane-aided Organic Acid Esterification

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Abstract. Esterification is a common route to produce carboxylic acid esters as important intermediates in chemical and pharmaceutical industries. However, the reaction is equilibrium limited and needs to be driven forward by selective removal one of the products. There have been some efforts to selectively remove water from reaction mixture via several separation processes (such as pervaporation and reactive distillation). Integrated pervaporation and esterification has gained increasing attention towards. Inorganic zeolite is the most popular material for pervaporation due to its high chemical resistant and separation performance towards water. Zeolite also has proven to be an effective material in removing water from organic compound. Zeolite can act not only as selective layer but also simultaneously act as a catalyst on promoting the reaction. Hence, there are many configurations in integrating zeolite membrane for esterification reaction. As a selective layer to remove water from reaction mixture, high Si/Al zeolite is preferred to enhance its hydrophilicity. However, low Si/Al zeolite is unstable in acid condition due to dealumination thus eliminate its advantages. As a catalyst, acid zeolites (e.g. H-ZSM-5) provide protons for autoprotolysis of the carboxylic acid similar to other catalyst for esterification (e.g. inorganic acid, and ion exchange resins). There are many studies related to zeolite membrane aided esterification. This paper will give brief information related to zeolite membrane role in esterification and also research trend towards it.

1. Introduction

Esters have a lot of important applications in industry mainly for fragrances and flavors. For example, combination of esters with other organic compounds will resemble fruit flavors [1]. Esters are also used in the synthesis of polymers (such as the Dacron[®] polymer), medicines [2] and biodiesels [3]. Generally, esters are produced via esterification reaction [4].

Esterification of organic acid with alcohol is an example of equilibrium-limited reaction. To drive the reaction to favor the product formation, an excess of alcohol can be used. However, the usage of excess alcohol requires further separation process and increase the operation cost. Another approach to enhance the reaction is via water removal from reaction mixture using reactive distillation or membrane processes such as pervaporation (PV) and vapor permeation (VP). PV and VP offers more efficient energy usage and environmentally friendly.

Nevertheless, both cases of membrane processes use a stirred tank type reactor that gives less capacity than a flow type reactor. Hence, PV system is difficult to be used in the reaction due to its direct contact with strong acid that damage the membrane layer unless solid catalysts such as zeolites and ion-exchange resins are employed. On the other hand, VP suffer from limited water fraction in the vapor phase is due to the gas-liquid phase equilibrium. After reaction, a post treatment to remove acid



from reaction mixture is required. However, there are no attempt to present vapor-phase esterification and in-situ water vapor separation in the flow-type membrane reactor. Because of the harsh condition, no zeolite membrane can withstand it [5].

During PV or VP, the permselective membranes are used to separate water from reaction mixture [6, 7]. The driving force of water permeance through membrane is the chemical potential gradient across the membrane. In the past decade, PV and VP have been proven effective for solvent dehydration and organic separation [8-10]. VP has the advantage of indirect contact between acid and membrane material plus usually VP has better flux than PV due to higher temperature employed. However, VP have higher energy requirement compared with PV in order to vaporize the reaction mixture or reactant prior to contact with membrane.

Membrane reactors employed to carry out equilibrium-limited esterification are an attractive alternative due to several reasons such as [11]:

- (1) Separation efficiency is not limited by relative volatility as in distillation
- (2) Only permeate change phase into vapor so that the energy consumption is lower than distillation
- (3) Pervaporation could be carried out at reaction temperature making it simpler in operation.

In the literatures, esterification reaction coupled with pervaporation usually was carried out in a batch reactor using homogeneous or heterogeneous catalyst [11, 12]. A part of reaction mixture is then fed into polymeric pervaporation membrane module, and refluxing the retentate to the reactor. This configuration has been used for many pairs of organic acid and alcohol such as acetic acid with methanol [13, 14] or borneol [15], oleic acid with various alcohols [16], and propanoic acid with propanol [17]. Some modifications have also been done to this configuration such as placing the membrane inside the reactor [18, 19], or enhancing the separation of water by the employment of adsorbent in the permeate side [20].

Among membrane materials, zeolite membranes have high permeability and chemical resistant suitable for esterification. Not only as selective layer, zeolites can also have a role as a catalyst for esterification. Esterification reaction mixture consists of water, alcohol, carboxylic acid, and catalyst. This reaction can gain benefit over selective removal of water from reaction mixture by pushing equilibrium towards product formation. Zeolite membrane's first commercial application was solvent dehydration especially ethanol dehydration. Water from Ethanol-water mixture can be effectively separated via pervaporation using zeolite membrane. Because of said reasons, zeolite membrane possesses a big potential to assist esterification reaction.

There are a lot of works related to organic acid esterification using zeolite membrane reactor. However to the best of our knowledge, there are currently no review paper that summarize research efforts in this field although the significance of the process. This paper will discuss general research trend related to zeolite membrane reactor concept for esterification of organic acid. Special attention will be given to the progress of zeolite selective layer

2. Membrane Reactor Concept for Organic Acid Esterification

Membrane technology has rapid development recently primarily due to its advantages and potential to various applications in various sectors [21-25]. Besides providing selective layer to one of reaction component, membrane can also play a role as catalyst support even active catalytically itself. Recently, integration of membrane and reaction vessel into membrane reactor (MR) has gained increasing attention. Some advantages in using membrane reactors are removal of an intermediate (or final) product, control of reactant addition, control gas and catalyst contact, and combine multiple reaction at the same system [26, 27].

A respective ester can be formed directly from an alcohol and a carboxyl acid by the addition of heat. This catalyst-free reaction is desirable because there is no catalyst to be separated from the reaction medium and products. Catalyst, mainly acid or base compounds, is usually employed to this reaction to enhance the reaction and eliminate the use of thermal energy,. The general esterification reaction is:



Because esterification is a reversible reaction, selective removal of reaction product(s) from reaction mixture can be beneficial to shift the reaction towards product formation. Pervaporation is a membrane based separation where a permselective membrane is in contact with a liquid mixture (feed) on one side and vacuum condition is applied to the other side to promote permeation of feed components. After permeating across the membrane, permeating compounds will be condensed in a cold trap. By selection of membrane type, it is possible to control which compound will permeate through the membrane and which compound that will remained as retentate stream [15].

Membrane reactors can be categorized by the catalytic activity of the membrane [28-33]. Catalytically active membranes work simultaneously as catalysts and separators while inert membrane reactors help the equilibrium of reaction only by removing the products or byproducts [34]. Hydrogen selective membrane for hydrogen production are more widely tested application of membrane reactor [35, 36], meanwhile water-permeable membranes are tested to study esterification reactions [37, 38]. Several membrane reactor configurations to carry away esterification reaction are depicted in Figure 1.

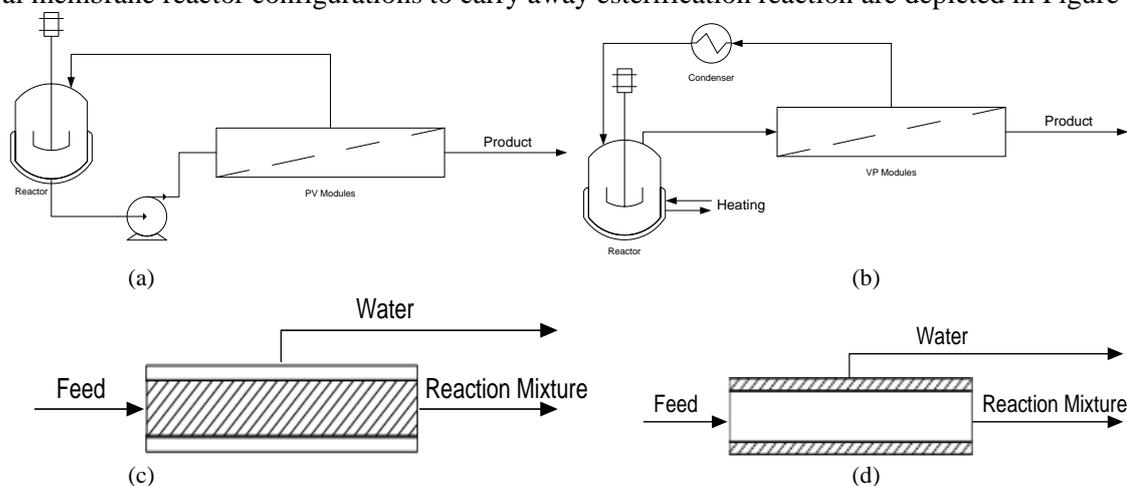


Figure 1. Different configuration of membrane reactor aided esterification reaction: (a) semi-batch pervaporation; (b) semi-batch vapor permeation; (c) Catalytic membrane reactor (d) Catalytically active membrane.

Zeolite membranes are suitable materials for membrane assisted esterification [38, 39] due to their potential in high permeability and high acid stability. For example, permeability of A-type zeolite membrane was found to be $0.14 \text{ mol m}^{-2} \text{ s}^{-1}$ for 78 mol% ethanol solution at 348 K [40]. However, the membrane has very low acid stability [41]. On the other hand, T-, MOR-, and SOD-type zeolite membranes have high acid stability [42-44]. Nevertheless, their permeation flux was much lower than A-type zeolite membrane. Membranes with high permeation flux and acid stability are necessary for membrane-assisted esterification [34].

3. Performance of Zeolite as Selective Layer

The main objective of zeolite selective layer in Esterification membrane reactor is to remove water from reaction mixture. Thus, hydrophilic zeolite membrane is desirable for this task. On the other hand, zeolite must sustain highly acidic reaction mixture condition due to organic acid and the presence of acidic catalyst. Said properties are related to Al content in the zeolite shown by its Si/Al ratio. While lower Si/Al ratio tend to produce more hydrophilic zeolite, serious dealumination by acid condition occur to zeolite that contain more Al [11]. This problem usually coped by using moderate Si/Al ratio zeolite or preventing contact between zeolite and reaction solution by vapor permeation.

During the last 20 years, zeolite membranes have gained increased attention to various applications. Simultaneously, their performances have been much improved in terms of permeance and selectivity. Popular zeolite framework used as composite membranes are LTA, FAU, MFI, etc. specifically, LTA have already been in practical use for solvent dehydration [45].

Table 1. Esterification performance carried out using zeolite membrane

Membrane	Catalyst	Temperature (°C)	Reactant	Organic Acid Conversion (%)	Water/reactant separation factor		Reference
					Alcohol	Acid	
MOR	H-ZSM-5	65	EtOH/H-Ac	22.8	2.9	2.6	[46]
LTA	PTSA	70	EtOH/H-Lac	>90	1,000	N/A	[39]
Zeolite T	Amberlyst 15	70	EtOH/H-Ac	>90	260	182	[47]
MOR	Amberlyst 15	85	EtOH/H-Ac	89.4	192	98	[11]
LTA	Amberlyst 15	85	EtOH/H-Ac	53.1	32	18	[11]
LTA	PTSA	81-92	IPA/H-Propionic	>90	200-10,000	N/A	[48]
CHA	H ₂ SO ₄	92	IPA/H-Adipic	88-89	N/A	N/A	[34]
SOD	Amberlyst 15	90	EtOH/H-Ac	>90	~10,000	N/A	[38]
Na-CHA	H-MOR	130	EtOH/H-Ac	76	2850	∞	[5]
MOR	H ₂ SO ₄	85	EtOH/H-Ac	76.76	N/A	852	[49]

Zeolite membranes have pores in the range of molecular sizes, which implies that they are capable of very specific interactions (e.g., selective adsorption, molecular sieving) with the target molecules. Moreover, their characteristics make them ideal candidates to integrate reaction and separation [28]. The available works that employ zeolite membrane reactors in esterification reaction mostly used a discontinuous configuration.

Tanaka et al. [47] used zeolite T membranes and Amberlyst-15 catalyst for esterification of acetic acid and ethanol. The result shows an acetic acid conversion of almost 100% after 8 h. Iglesia et al. compared mordenite and LTA membranes for esterification of acetic acid with ethanol using Amberlyst-15 catalyst in a continuous membrane reactor [11]. Mordenite and LTA was able to cross the equilibrium limitation in less than one day of experiment. Mordenite membranes showed better resistance to acid even after five days of experiment with high separation factors of H₂O/EtOH and H₂O/HAc. On the other hand, LTA conversion dropped dramatically due to the instability of the zeolite to acid condition.

As seen on Table 1, LTA, MOR, and CHA are common framework used as separative layer while Amberlyst or PTSA are common catalyst. The usage of MOR and CHA can be directly contacted with acidic reaction mixture due to its higher acid stability. However, their water/alcohol separation factor is relatively low compared with LTA membrane which is popular due to its high hydrophilicity and separation factor towards water. Nevertheless, the acid conversion of most work tend to approach completion in terms of high conversion at about >90% while at similar temperature the equilibrium conversion is about ~70%. On the other hand, the choice of catalyst favor ion exchange resin Amberlyst-15 or homogeneous catalyst. These catalysts show almost complete reaction with the assistance of zeolite membrane.

Continuous esterification reaction has been done by several authors mostly by employing membrane reactor. Overall, continuous reactor showed higher activity to batch or semi-batch process in steady state condition. An exception to this trend is when high Si/Al zeolite such as LTA was used. Some authors reported a huge decline in reactor performance after some time due to dealumination experienced by said framework [11]. Itoh et al. [5] studied continuous vapor permeation membrane reactor for esterification of acetic acid and ethanol. The reaction was carried out using various catalyst and CHA membrane at atmospheric temperature. The result suggest that H-MOR is the most active catalyst and both CHA and H-MOR have good durability over long term esterification reaction with no decline observed for 8 hour operation.

4. Zeolite as a Catalyst for Esterification

As for Esterification reaction catalyst, acid or ion exchange resins are usually used. These catalysts donate proton for the autoprotolysis of carboxylic acid. Previously, inorganic acids such as H₂SO₄, HCl, HI or ClSO₃OH [50, 51] or organic acids such as p-toluene sulphonic acid (PTSA) [39, 52] are used to perform the reaction. Base catalyst may also be used with additional formation of long chain soaps [53]. However, the use of homogeneous catalysts in chemical industry are no longer interesting since they are miscible with reaction medium even though they have lower cost and higher performance. Their miscibility with reaction medium causes more problems such as additional needs of downstream separation process and also corrosion of devices in contact with the acid. Therefore, heterogeneous catalysts such as ion exchange resins [54-58], and zeolites [59-61] have gained increasing attention to carry away esterification reaction. Zeolites for esterification catalyst are popular to upgrade bio-oil into biodiesel or for hydrotreating feed [62-64]. Among zeolites, MFI and FAU, especially zeolite Y, are the most popular framework for esterification reactions. The performance of zeolite depends mainly on their acidity and pore size related with mass transfer of reactants. Peters et al. [61] compares catalytic activity of various catalyst for the esterification of acetic acid with butanol. The best result in terms of activity was gained for ion exchange resins, followed by sulphated zirconia and zeolites. The results also show that zeolite H-USY (with Si/Al=20) has the highest activity among zeolites [11].

Kirumakkin et al. [65] compared the performance of H β , HY, and HZSM5 zeolite for esterification of benzyl alcohol with acetic acid. The result showed that the conversion follows the order of H β >HY>HZSM5. The conversion of H β reached 75% at 130°C while the other zeolite performance capped around 60% conversion. However, ester selectivity over ether formation is better using HZSM5 zeolite where the pores are smaller than H β and HY. H β and HZSM5 have stronger acidity compared with HY that they possess higher potential in catalyzing esterification reaction [66]. It is widely accepted that esterification activity using zeolite catalyst is affected by surface acidity and pore structure related to reactant mass transfer. Different reactants and/or product may have different optimum framework to carry away the reaction. In addition, for catalytically active membrane, different framework might have to be prepared as distinguish layers because separation performance of highly active framework might not be sufficient.

5. Summary and Future Outlook

General aspects of zeolite membrane aided organic acid esterification have been reviewed. Zeolite not only has role on removing water from reaction mixture but also catalytically boost the reaction kinetics. A lot of works have shown the effectiveness of zeolite based membrane reactor to substitute conventional processes. Hopefully, the aid of zeolite membrane can be implemented to the synthesis of various esters.

In the future, this technology needs some improvement in the subject of membrane (materials, methods, and reproducibility), and cost optimization (mainly for industrial implementation). The numbers of researches that study various aspects of this technology suggest that it is ready for further industrial implementation. Nevertheless, the implementation of this technology depends mainly to energy source cost because its main advantage lies on lower energy consumption compared with conventional separation systems [67].

Further study on membrane material, configuration, and catalyst selection for various type of target ester should be done to quantitatively and economically reflect the progress of zeolite membrane aided organic acid esterification to be implemented in industry.

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