



Coupling of in-situ pervaporation for the enhanced esterification of propionic acid with isobutyl alcohol over cenosphere based catalyst



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ABSTRACT

In the present work, pervaporation assisted esterification of propionic acid and isobutyl alcohol, to produce isobutyl propionate and water was investigated in an in-situ type pervaporation reactor. A commercial polymeric hydrophilic PVA-PES membrane was used to shift the conversion of equilibrium limited esterification reaction by the removal of water from the reaction mixture. Catalyst developed from cenosphere (waste material) was used in the study. The effects of process parameters viz; reaction temperature, catalyst loading, alcohol/acid molar ratio and a ratio of effective membrane area to initial reaction volume (S/V) were studied.

Catalyst characterization elucidated that the catalyst exhibited significant silica content, surface acidity with a considerable surface area. The membrane showed a significant selectivity towards the water removal which subsequently enhanced the pervaporation performance. A substantial enhancement in the conversion of esterification reaction from 67% to 88% was observed by the incorporation of pervaporation at a temperature of 353 K. The membrane and catalyst revealed a significant stability up to four and three reaction runs respectively. Results revealed that all process parameters linearly affected the conversion and permeate flux of pervaporation assisted esterification. The maximum esterification conversion was obtained to be 92% at a reaction temperature of 353 K, catalyst loading of 20 g/L, alcohol/acid molar ratio of 2.5 and S/V ratio of 19.63 m⁻¹.

1. Introduction

In the recent years, the membrane based separation processes has attracted much attention in the chemical industry. Production of esters is one of the typical applications of membrane based process. The esterification reaction produces water as by-product which affects the activity of catalyst and reaction rate [1]. Typically, esterification reactions are kinetically and thermodynamically limited [2] and the equilibrium can be shifted towards the ester production by two ways; (i) large excess of one of the reactants; (ii) removal of one or more product species from reaction medium. The former is an uneconomical approach as it requires large reactor volume which, subsequently will lead to increase in the cost of equipment [3]. The latter approach can be incorporated by using a hybrid process in which the reaction and separation can be possible. Among hybrid processes, reactive distillation was employed for simultaneous reaction and separation. However, in the distillation step, the product gets hydrolyzed due to the trace water and thereby reduces the purity, quality and usability [4]. In spite of using traditional distillation process, membrane based separation process such as pervaporation is more promising because of higher compactness, higher selectivity and lesser capital cost [5]. Additionally, in

pervaporation the energy consumption reduces by 75% while the investment and operating cost decrease by 50% as compared with reactive distillation [6]. Pervaporation is used for continuous removal of one the product species from reaction mixture, generally water to shift the reaction conversion beyond equilibrium and it is proved to be an efficient technique due to its lower energy requirements and ability to separate azeotropic mixtures. The selective removal of water from reaction medium as soon as it is formed will lead to the catalyst to perform effectively which obviously enhances the ester conversion. Thus, coupling of esterification with pervaporation has drawn a great attention in recent years [7–9].

Pervaporation has been investigated in thermodynamically limited esterification reactions in most of the recent studies. Sert et al. studied the esterification combined with pervaporation of acrylic acid and *n*-butanol using Amberlyst-131 catalyst and hydrophilic Pervap 2201 membrane [10]. The ester conversion successfully enhanced by removing water from the reaction mixture through Pervap 2201 membrane. Han et al. studied the pervaporation coupled esterification of oleic acid with ethanol using NaA zeolite membrane [11]. The membrane showed a good performance up to eight runs in pervaporation assisted esterification. Zhang et al. prepared the catalytically active

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Nomenclature

J_i	Partial fluxes of components (mol/m ² h)	C_w	Concentration of water in permeate (mol/L)
y_i	Weight fraction of the component in permeate	δ_t	Total HSP value (MPa ^{1/2})
J	Total permeate flux (mol/m ² h)	δ_d	Contribution of HSP by dispersion (MPa ^{1/2})
W	Weight of permeate (mol)	δ_p	Contribution of HSP by dipole moment (MPa ^{1/2})
S	Effective membrane area (m ²)	δ_h	Contribution of HSP by hydrogen bonding (MPa ^{1/2})
t	Reaction time (min)	J_e	Pre-exponential factor (mol/m ² h)
J_w	Water permeation flux (mol/m ² h)	E	Activation energy (kJ/mol)
V	Volume of reaction mixture (L)	T	Absolute temperature (K)

pervaporation membrane and investigated it in pervaporation coupled esterification of acetic acid and *n*-butanol [12]. The membrane consisted of three layers upper catalytic layer, middle selective PVA layer, and bottom PES support layer. The conversion was significantly enhanced by using the membrane with good catalytic membrane stability. The pervaporation assisted esterification of acetic acid and ethanol by using prepared mordenite membrane was investigated which showed a good performance up to eight successive reaction runs [5]. Additionally, several studies related with significant application of pervaporation for the esterification reaction were reported in the last decades [13–20].

Nowadays, heterogeneous catalysts are preferred over homogeneous catalysts in the esterification reactions due to various limitations associated with the use of homogeneous catalysts [21,22]. The heterogeneous catalysts have advantages of stability, recyclability, product purity and are easy to separate from the reaction mixture [23]. Various commercial catalysts are available for the esterification reactions and their studies have been reported in the literature [24–28] however, the utilization of waste material for the esterification assisted pervaporation has not been reported so far. In the present work, the catalyst was developed from cenosphere which is a by-product of thermal power plants in order to minimize the operating cost of pervaporation process.

Isobutyl propionate is a colorless liquid having a characteristic fruity odor reminiscent of apple, apricot, and rum. It is less dense than water and soluble in alcohol, ether, and many organic solvents. It has wide application in the food industry as artificial flavor and fragrance. In the previous work, isobutyl propionate was synthesized in an ex-situ type pervaporation reactor using *p*-toluene sulfonic acid [29]. The esterification reaction was performed in glass reactor whereas the separation of water from the reaction mixture was carried out in a pervaporation module fitted with a hydrophilic membrane. Both reaction and separation was performed in separate units and hence the name ex-situ type reactor. However, in the present study, production of isobutyl propionate was carried out in an in-situ type pervaporation reactor by employing heterogeneous catalyst developed from cenosphere. Here, the reaction and separation were carried out in a single unit provided with a hydrophilic membrane. The advantage of using in-situ type reactor is its compactness and low energy requirements. The effects of various process parameters namely reaction temperature, catalyst loading, alcohol/acid molar ratio and the ratio of effective membrane area to initial reaction volume (S/V) were extensively investigated. The influence of membrane on the equilibrium shift of the reaction was also considered and membrane flux of each component for each process parameters was evaluated. Moreover, the performance of pervaporation, the stability of membrane and catalyst were investigated.

2. Experimental

2.1. Materials and chemicals

A commercial hydrophilic PVA-PES membrane supplied by Permionics Membranes Pvt. Ltd. (Gujarat, India) was used in the study.

The operating pH of the membrane was ranged from 2 to 9. The effective membrane area was 0.0785 m² and membrane thickness was 250 μ m. Cenospheres was supplied by Vipra Ferro Alloy Pvt. Ltd. (Maharashtra, India) which mainly composed of SiO₂, Al₂O₃, and Fe₂O₃ (> 70%). Propionic acid and ethanol were obtained from Merck. Conc. H₂SO₄ was procured from Fisher Scientific, India. Methanol and Karl Fischer reagent were purchased from Rankem Chem. Ltd. (Mumbai, India) and *n*-hexane (GC grade) was purchased from Sigma-Aldrich. All chemicals used in this study were of analytical reagent grade and used without further purification. Deionized, double distilled water was used in all test work.

2.2. Catalyst synthesis and characterization

The cenosphere supported solid acid catalyst was prepared by employing wet impregnation method. Firstly, the collected cenosphere was sieved to a size of < 100 μ m. The impregnation was started by loading cenosphere powder with different wt% of conc. H₂SO₄. The measured amount of cenosphere powder was loaded with the known amount of aqueous solution of conc. H₂SO₄. The obtained mixture was agitated in a proper manner to fill up the pores of cenosphere and then dried in a hot air oven for 2 h at 363 K. The resultant cenosphere powder was then transferred to silica crucible and placed in muffle furnace at 543 K for 4 h for calcination. Typically, for 10 g of cenosphere, 10.1 mL aqueous solution of 40 wt% of conc. H₂SO₄ was required. After calcination, the obtained cenosphere powder was cooled to room temperature and stored in air tight storage bottle.

The cenosphere supported solid acid catalyst was characterized by FESEM, FTIR, BET and surface acidity. The morphological analysis of untreated cenosphere and cenosphere supported solid acid catalyst was examined by FESEM (Hitachi, S-4800, Japan) at 15 kV at a magnification of 1500X. The material was coated with thin film of gold before taking a micrograph. FTIR equipped with ATR (Thermo Scientific iD5) was used for the spectroscopic analysis of untreated cenosphere and cenosphere supported solid acid catalyst. The FTIR analysis was carried out in the range of 400–4000 cm⁻¹.

The surface area analysis of untreated cenosphere and prepared catalyst were investigated by BET (Smart Instruments Co. Pvt. Ltd., Mumbai, India) single point method via nitrogen adsorption/desorption method. The method of titration was used to evaluate the number of active acidic sites present in the catalyst. For this analysis, 1 g of dried prepared catalyst was mixed with 50 mL of 1 M sodium chloride solution and sonicated at room temperature for 1 h. The catalyst was then filtered out and the remaining solution was titrated against 0.1 N sodium hydroxide solution using phenolphthalein indicator.

2.3. Pervaporation experiments

The pervaporation (PV) assisted esterification experiments were performed in an in-situ type stainless steel PV reactor with 2 L capacity (Shivohm Membrane systems, Maharashtra, India) as shown in Fig. 1. The membrane was placed at the bottom of reactor and the feed was introduced into the PV vessel. It was heated up to desired temperature

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