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Research paper

Process intensification of esterification reaction for the production of propyl butyrate by pervaporation

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Abstract

Pervaporation is a membrane separation process vastly used for purification in chemical and allied industries. Esterification reaction can be intensified and enhanced by coupling with pervaporation reactor (PVR). Polyvinyl alcohol (PVA)/polyethersulfone (PES) composite membrane was used for the pervaporation coupled esterification reaction study. Esterification of butyric acid with n-propanol was taken as a model reaction for the study and to test the performance of pervaporation reactor. Catalyst p-toluenesulfonic acid was used for the esterification reaction. The effects of various reaction parameters on conversion of butyric acid such as reaction temperature, initial molar ratio of n-propanol to butyric acid, catalyst loading and reaction time were studied. Experimental results show that the increase of temperature, initial molar ratio, and catalyst concentration enhance the conversion of butyric acid considerably. The highest conversion of 96.41% was obtained at temperature 353 K, molar ratio of 2 and catalyst loading of 2.5%w/w at reaction time of 420 minutes. PVA/PES membrane used in the experiments shows the good activity and hydrophilicity and plays a vital role for enhancing the conversion by selectively removing water. Pervaporation coupled esterification shows the better choice over the conventional route for the production of esters. This technique is environment friendly and energy intensified approach as it reduces pollution and energy requirement.

Keywords: Esterification; Pervaporation reactor; Composite membrane; Butyric acid; n-Propanol

1. Introduction

Energy consumption in the world increased tremendously over the recent years because of human being and population's and daily needs. For sustainable development, there must be minimum energy consumption giving maximum benefits to human life and environment. This can be achieved by using clean, green, and renewable energies in industries and can be minimizing energy consumption by using process intensification, hybrid technology, novel equipments, and techniques that can be transformed energy into clean, safer, and environmental friendly energy [1]. The separation and purification technology has the advantages to produce useful products or to recover useful materials from the waste by the separation processes like reactive extraction, adsorption, and pervaporation [2–7]. These separation processes contribute in major areas of separation in chemical and its allied industries. Esters are very important class of chemicals used in human day to day life as it contains aroma. Organic esters have many important applications in chemical and allied industries such as in food industries for flavor and fragrance, as solvents, plasticizer in polymer industries, as insulator in power industries [8–10]. Esters are formed by esterification reaction between acids and alcohols in presence of homogeneous catalyst such as H_2SO_4, HI, HCl or heterogeneous catalyst such as Amberlyst, Dowex resins [8,11–15]. Esters can be produced in batch, semibatch and continuous mode of operation [16,17]. Esters were also produced in various designed reactors and processes such as conventional distillation, reactive distillation (RD), micro reactor and packed bed reactor (PBR) [18–20]. Distillation and packed bed reactors consumed high energy depend on vapor–liquid equilibria of the system and required number of separation units for the product separation and handling the azeotrope. Alternative to these methods, pervaporation was used for ester production because of simple design, less energy consumption

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Nomenclature

A	Butyric acid
B	n-Propanol
E	n-Propyl butyrate
W	water
k_1	forward reaction rate constant ($lit.mol^{-1}.hr^{-1}$)
k_2	backward reaction rate constant ($lit.mol^{-1}.hr^{-1}$)
J	flux through the membrane ($Kg.m^{-2}.hr^{-1}$)
W_P	weight of water collected (Kg)
A_P	effective membrane area (m^2)
Δt	time interval difference (hr)
MR	molar ratio (n-Propanol/Butyric acid)
CL	catalyst loading (wt%)
T	temperature (K)
BR	batch reactor
PVR	pervaporation reactor
PVA/PES	polyvinyl alcohol/polyethersulfone
[BA]	concentration of butyric acid ($mol.lit^{-1}$)
[PB]	concentration of n-propyl butyrate ($mol.lit^{-1}$)
C_W	concentration of water ($mol.lit^{-1}$)

and can operate beyond vapor–liquid equilibrium and can easily handle azeotropes [21–23].

Pervaporation is extensively used in chemical industries for separation of chemicals. Pervaporation coupled with esterification reaction is energy intensified approach as it uses less energy consumption compared to conventional distillation, reactive distillation column (RDC) and packed bed reactor (PBR). Nowadays, membrane reactors played vital role in separation and purification process because of high selectivity of membrane and it does not depend on vapor–liquid equilibrium [24]. Esterification is reversible and equilibrium limited reaction and hence conversion of reactants was limited because esterification reaction is thermodynamically equilibrium in nature. Pervaporation could drive the equilibrium reaction such as esterification, synthesis of methylisobutyl ketone and etherification [25–27]. Pervaporation can enhance the conversion of acid because of one of the product (water or ester) of the esterification reaction continuously removed by the membrane [28,29]. Polyvinyl alcohol (PVA) and its composite catalytic membranes have several advantages in pervaporation for esterification and dehydration of solvents because of high hydrophilicity, high flux and less swelling [30–33].

In the present study, butyric acid and n-propanol were taken as model system for esterification reaction coupled with pervaporation. Polyvinyl alcohol (PVA)/Polyethersulfone (PES) composite membrane was used for the study. Esterification reaction was catalyzed by using catalyst p-toluenesulfonic acid. Effect of various parameters such as reaction temperature (323 K, 333 K, 343 K and 353 K), molar ratio (n-propanol/butyric acid = 1, 1.3, 1.7 and 2), catalyst loading (1, 1.5, 2 and 2.5%w/w) and reaction time on conversion of butyric acid were studied.

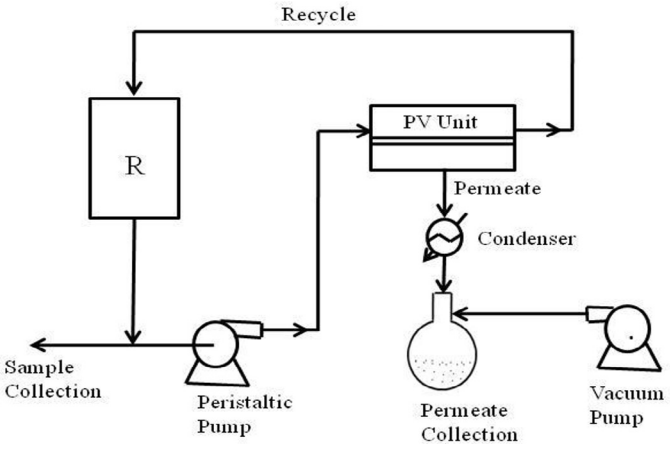

Fig. 1. Lab scale experimental set up of esterification reaction coupled with pervaporation reactor.

2. Materials and methods

2.1. Chemicals and reagents

Butyric acid (99% purity) and oxalic acid (99.8% purity) was supplied by S. D. Fine Chem Ltd., Mumbai, India and n-propanol (99% purity), p-toulenesulfonic acid (98% purity), sodium hydroxide pellets (EMPARTA) and phenolphthalein indicator were supplied by Merck India Ltd., Mumbai, India. In this study, p-toulenesulfonic acid is used as catalyst which is white solid in nature. It is a strong acid having sulfonic group attached to the ring. p-Toluenesulfonic acid is soluble in water, most of the alcohols and other polar solvents. Polyvinyl alcohol (PVA)/Polyethersulfone (PES) composite membrane was supplied by Permionics Membranes Pvt. Ltd., Baroda, India. All purchased chemicals and reagents were used without pretreatment and purification.

2.2. Experimental set up

Esterification reactions of butyric acid with n-propanol coupled with pervaporation reactor and without pervaporation were carried out in batch mode of operation. Experimental set up of the reaction is shown in Fig. 1. Reactor (R) made up of stainless steel (MOC, SS-316) surrounded by jacket having capacity of three liter volume was used as a batch reactor. Heating was provided by heating coil placed at the bottom of the reactor, and temperature of the reaction was sensed by the sensor and controlled by the PID (Proportional-Derivative-Integral) controller. The resolution of temperature is 0.1°C and accuracy of temperature controller is ±0.5°C. Reactor (R), peristaltic pump, pervaporation (PV) unit, vacuum pump and condenser (with attached chiller) were the major components of the experimental set up. Pervaporation coupled esterification experiments were conducted in batch reactor and pervaporation reactor (PVR). Reactor (R) served both as batch reactor and pervaporation reactor. By switching off peristaltic pump and vacuum pump, reactor acted as a batch reactor and by switching