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Novel esterification reaction from biomass product by coupled acetate membrane and catalysts for ethyl lactate separation

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ABSTRACT

This study presents the effect of combined membrane separation and heterogeneous catalysts for the production of ethyl lactate solvent. The enhanced process is a flat sheet cellulose acetate membrane and cation-exchange resin catalysts. A methodology based on catalyst and acetate membrane impregnation in the presence of a sweep gas at low pressure with the aim of obtaining a higher yield of the ester product have been developed. The esterification reaction was carried out at the temperature of 60 °C. The ester product gave a percentage yield of up to 75%. The ion chromatogram of the ester product obtained in the catalyst and membrane impregnation was compared with the esterification product of the batch esterification reaction. The gas chromatograph NIST library spectra of the ester product indicated the structure of ethyl lactate (45) on the mass spectra which was in accordance with the commercial ethyl lactate. Products obtained on dowex 50W8x and amberlyst 36 resin catalysts were found to elute faster at 1.503 and 1.527 min respectively in contrast to those using amberlyst 15 and amberlyst 16. In all, the percentage yield of the ethyl lactate can be improved using cellulose acetate membrane. Amberlyst 36 and dowex 50W8x cation-exchange resins were revealed as the most effective catalysts for the esterification process involving lactic and ethanol to produce ethyl lactate in contrast to other cation-exchange resins that were used in the study. The results further confirms effectiveness of cellulose acetate membrane in the selective removal of the water from the esterification product.

Introduction

The world's energy consumption has increased tremendously over the recent years due to increase population and daily requirement. For sustainable development, there must be minimum energy consumption giving maximum benefits to human life and environment. This can be obtained via green, clean, and renewable energies in industries which can reduce energy consumption by using process intensification, hybrid technology, novel equipment and techniques that can transform energy to clean solvents. The separation and purification technology has the advantages to produce useful products or to recover useful materials from the waste by the separation

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processes such as reactive extraction, adsorption and pervaporation [1]. The development of renewable fuels has attracted a lot of attention over the last few years due to the depletion of petroleum reserves and increased environmental concerns [2]. Ethyl lactate has shown a lot of promise as a powerful non-toxic replacement for toxic, halogenated and petroleum-based solvents such as toluene, hexane, *n*-methylpyrrolidone (NMP), acetone and xylene [3,4], that have dominated U.S.A and the world market over the years [5,6]. In the past decade, there has been an increasing demand for using bio renewable materials instead of petroleum based feedstock for the production chemicals, driven by environmental concerned and sustainability. Research has shown that bio-based product is one of the major pillars of the sustainable economy. However, nature produces over 170 billion tons of the biomass products per year by means of photosynthesis. Out of this, 75% of these products belong to the carbohydrates, while 3–4% of these compounds are used by humans for food and non-food purposes [7]. Biomass products are organic matters in which solar energy is stored through chemical bonds including trees, crops and animal manure. In contrast to other renewable energy sources, biomass is the only renewable feedstock that can be converted into energy and chemical products. Esterification reaction is widely used in the chemical industries. However, esters can be classified into different category ranging from aliphatic to aromatic with various substitutions and multifunctional groups. Different synthesis routes have been used for the production of esters, but most of these do not meet the standard that is applied in the chemical industry. Recently, the synthesis of alkyl esters of lactic acid including ethyl lactate has attracted a lot of attention due to the fact that they can be obtained from renewable sources. A lot of work have described this synthesis by heterogeneous catalysis using amberlyst 15 heteropolyacids and dowex 50W, however, the process is limited by equilibrium resulting in a conversion of only 35% [6]. Alkyl lactates are high boiling point liquids and can be used as solvents and plasticizers for cellulose plastics and vinyl resins, among other applications. They also take part in cosmetic and herbicidal formulations and are used as skin whitening products. Esterification of an acid catalyzed reaction which traditionally is carried out over mineral acids. The problem is that these catalyst are corrosive, toxic, non-reusable and often hard to remove from the products. This problem can be overcome by the used of a solid acid catalyst including heterogeneous catalysts. Many of the solid acid catalyst cause a lot of drawback including poor thermal stability, poor regeneration ability, low turnover numbers and low specific surface area [2]. Maximizing the reaction conversion at equilibrium (which represents the maximum attainable conversion) is one of the most significant criteria for reaction optimization as well as catalytic activity, selectivity and kinetics. Indeed, maximizing the equilibrium conversion needs a large number of experiments to be carried out in order to screen all operating conditions including the nature of solvent, the solvent phase volume ratio, the initial substrate concentration, the pH and temperature needed. To overcome these problems, various predictive methods which explains the thermodynamics for reactions in two-phase media have been developed in order to evaluate conversion at equilibrium [8]. Ethyl lactate can be produced from the reversible esterification of biomass fermented ethanol and lactic acid. Besides the numerous applications, esters from nonedible crops and alternative sources are potential candidates in carbon emission reduction. In order to ascertain the future energy supplies and offset the environmental impact, low-carbon technologies will play a major role with this regards [9]. Biomass-based feedstock provides a more sustainable alternative, but conversion possibilities and technologies must be realized to offer practical and economically possible sources of production [10]. Hydrogen is an important industrial feedstock for the production of fuels and other chemical, fuel cell applications and purification of hydrogen is an important unit operation. Hydrogen separation using membranes has emerged as an important technology and inorganic membrane has attracted a lot of application in hydrogen separation in contrast to polymeric membrane with limited permeance and selectivity [11]. Esterification reactions with both membranes and heterogeneous catalyst can be carried out at different temperatures in the presence and absence of a catalyst. Membrane reactors can incorporate both separation and reaction in one single unit. It can also be described as an intensive reactive system [12]. Membrane-based separation technologies has been successfully employed over the years in several industrial applications [13] including food, biotechnology, pharmaceutical and in the treatment of industrial effluents and has also replaced a lot of conventional technologies due to a number of advantages including reliability, simple to operate, absence of moving parts and ability to tolerate fluctuations in flow rate and feed composition [14]. Membrane technology has attracted a lot of attention from several industrial sectors and academics in their research due to the fact that the technology gives the most relevant means of reducing costs and environmental problems [15]. The use of membranes to selectively eliminate water from the reaction product during esterification of lactic acid is yet another important application that has attracted a lot of attention [16,17]. Generally, esterification reactions are usually limited by equilibrium and therefore do not reach completion [18,19], Although the traditional method of solving equilibrium problems in esterification reactions involve the addition of an excess amount of alcohol to the reaction system however, using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by in-situ removal of water from the reaction mixture [16].

Process intensification is defined as the improvement of a process at different scales and units of operation [20]. In the pervaporation membrane process, a thin polymer film is brought in contact with liquid solvent (feed) and permeate which dissolves and permeate through the membrane by diffusion mechanism along a concentration gradient. Although the transport behaviour of gases through a membrane is the same as that of porous ceramic membrane, the transport of gases through polymeric membrane depends on several factors including the nature of the polymer material, nature of crosslinks, cross link density and the temperature of the polymer. Among the different factors, the most predominant factor that strongly affects the transport process is the nature of the polymer material [21]. The permeate vapour can be condensed and collected or release as desired. The chemical

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