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Biodiesel production by quaternized polysulfone membrane: Experimental and kinetics model

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Abstract

The quaternized polysulfone catalytic membrane as a heterogeneous catalyst was used for producing biodiesel from continuous transesterification of soybean oil and methanol in flow-through catalytic membrane reactor. A kinetic model of transesterification for describing the transesterification was established. The conversions obtained from established model are in good agreement with the experimental data. The kinetics model of membrane can well predict the transesterificaton conversion.

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Keywords: quaternized polysulfone membrane; flow-through catalytic membrane reactor; kinetics model

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1. Introduction

With the gradual exhausting of the petrochemical resources and increasingly serious environmental problems, the exploration of a substitute becomes urgent. Among all the potential alternatives, biodiesel which is generally composed of fatty acid methyl ester (FAME) is believed as a promising one [1]. The biodiesel is commonly produced through transesterification of the oil and methanol using the homogenous or heterogeneous catalytic reaction by acid, alkaline or enzyme. Base-catalyzed transesterification is much faster than acid-catalyzed. Although homogenous base catalysts have fast reaction rate under mild reacting condition, some severe drawbacks of the catalysts are still obvious, such as severe corrosion, separation difficulties of catalyst from the product and the environmental problem derived from the liquid wastes discharge.

These complications could be overcome through the use of heterogeneous catalysts such as strong ion-exchange resins [2]. Fixed bed reactors packed with ion-exchange resins are most frequently used for heterogeneously catalyzed esterfication for producing biodiesel. However, particle attrition resistance, high pressure drop and low diffusional mass transfer limit the utility of this process [3]. An ideal alternative would be flow-through catalytic membrane reactor (FTCMR), as one of membrane reactors

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[4]. In the FTCMR, the advantages of the ion-exchange resins could be reserved. And a higher efficiency in mass transfer and catalysis could be achieved because of a close contact between catalyst and reactants in flow-through mode compared with ion-exchange resins. In the FTCMR, an unselective porous catalytic membrane is applied. And the membrane itself contains catalytic active components and the reactants were forced to flow through the pores membrane. The intensive contact between reactants and catalytic active sites result in high catalytic efficiency. Such catalytic membranes have shown great promise for a number of important reactions, such as isomerization, hydrogenation, dehydrogenation, oxidation, esterification, transesterification and so on [5].

In order to further analyze the reactive process and control the reaction parameters, the kinetics of the reactions in the catalytic membranes was also investigated. Shah and Ritchie [6] studied the kinetic process of esterification in a PES nanofiltration membrane containing sulfonic acid groups onto the pore surface. The kinetic model for the membrane catalyst in a flow-through system was developed to predict the catalytic behavior of membrane catalyst as a function of catalyst mass, reactant molar ratio and temperature. The model results fit reasonably well with the experimental data. The model could be also applied to predict the performance of the membrane catalyst for similar reactions.

The aim of the present work is to prepare a catalytic membrane from quaternized polysulfone as a heterogeneous catalyst to produce biodiesel by the continuous transesterification of soybean oil with methanol in a flow-through catalytic membrane reactor. Simultaneously, a mathematical model would be developed to elucidate the relationships between the catalytic membrane structure and its performance on the basis of theory calculation and experimental data of the continuous transesterification.

The thickness, area, porosity and the number of active sites of the catalytic membranes were taken into account in the kinetic study. The effects of internal and external mass transfer resistances on the transesterification were investigated. Finally, a kinetic model involving catalytic membrane structure and mass transfer of reactants in the FTCMR was established to predict the conversion.

2. Materials and Methods

2.1. Materials

PSF (PSU P-3500) was purchased from SOLVAY (America). Chloromethyl ether, anhydrous zinc oxide, trimethyl ammonium, N-methyl-2-pyrrolidone (NMP), potassium hydroxide and methanol were purchased from Tianjin Kermel Chemical Reagents Limited Company (Tianjin City, China). The chemicals were all analytic reagent (AR) grade and used without further purification. Soybean oil was purchased from Tianjin Jiali grainoil Co. Ltd., Tianjin City, China.

2.2. Preparation of quaternized polysulfone

The preparation process of quaternized polysulfone includes two steps: chloromethylation and quaternization. The procedures were briefly described as follows: PSF was first dissolved in dichloromethane and stirred for 0.5 h to form a homogeneous solution. Then, chloromethyl ether and anhydrous zinc oxide were added into the solution and stirred to catalyze the reaction. The resulted mixture was precipitated with methanol. The product was dried at 343.15K under vacuum for 24 h and chloromethylated PSF (CMPSF) was finally obtained. CMPSF was dissolved in 35% trimethyl ammonium solution at temperature range from 298.15 to 328.15 K for several hours.

2.3 Preparation of quaternized polysulfone membrane

The quaternized polysulfone membrane was prepared through the method of solvent evaporation phase inversion. The quaternized polysulfone was completely dissolved in NMP until a homogeneous polymer solution was formed. The solution obtained was cast carefully onto stainless steel plate. Then the plate was dried by evaporation at atmosphere for 24 h and the quaternized polysulfone membrane was obtained. The nascent quaternized polysulfone membrane was soaked in a 1.0 M potassium hydroxide aqueous solution at room temperature for 24 h, followed by washing with deionized water several times and immersing in deionized water prior to use.

2.4 Transesterification by membrane in FTCMR

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