



Continuous esterification to produce biodiesel by SPES/PES/NWF composite catalytic membrane in flow-through membrane reactor: Experimental and kinetic studies

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HIGHLIGHTS

- ▶ The conversion obtained by CCM was over 98.0% during the continuous esterification.
- ▶ The external mass transfer resistance was related to the flow rate.
- ▶ The internal mass transfer resistance was related to the membrane thickness.
- ▶ A kinetic model was established to predict the conversion.

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ABSTRACT

A novel composite catalytic membrane (CCM) was prepared from sulfonated polyethersulfone (SPES) and polyethersulfone (PES) blend supported by non-woven fabrics, as a heterogeneous catalyst to produce biodiesel from continuous esterification of oleic acid with methanol in a flow-through mode. A kinetic model of esterification was established based on a plug-flow assumption. The effects of the CCM structure (thickness, area, porosity, etc.), reaction temperature and the external and internal mass transfer resistances on esterification were investigated. The results showed that the CCM structure had a significant effect on the acid conversion. The external mass transfer resistance could be neglected when the flow rate was over 1.2 ml min^{-1} . The internal mass transfer resistance impacted on the conversion when membrane thickness was over 1.779 mm. An oleic acid conversion kept over 98.0% for 500 h of continuous running. The conversions obtained from the model are in good agreement with the experimental data.

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1. Introduction

Functional porous membranes with catalytic active components have recently attracted considerable attention in biodiesel production because the membranes are capable of eliminating equipment corrosion, easily separating the catalysts from the reactants, diminishing wastewater effluent by comparison with liquid acid process (Gröchel et al., 2005; Zhu et al., 2010). Further, the functional membranes have successfully been applied in a flow-through catalytic membrane reactor (FTCMR) (Schmidt and Schomäker, 2007). In FTCMR, the reactants were forced to flow-through the membrane pores. Each pore could be considered as a

micro-reactor. The intensive contact between reactants and catalytic sites in the membrane resulted in high catalytic activity (Fritsch and Bengtson, 2006; Purnama et al., 2006). Such catalytic membranes in FTCMR have shown very high catalytic efficiency as well as great promise for a number of some important reactions, such as isomerization, hydrogenation, dehydrogenation, oxidation, esterification and so on (Lopez et al., 2006; Shah and Ritchie, 2005). Lopez et al. (2006) immobilized sodium tungstate (Na_2WO_4) on plasma-treated poly(vinylidene fluoride) (PVDF) membrane surface as a flat membrane reactor for the oxidation of secondary amines to nitrones. The amine conversion of 100% within less than 3 h was achieved. Shah and Ritchie (2005) introduced sulfonic acid groups onto the pore surface of polyethersulfone (PES) nanofiltration membrane to catalyze the esterification between ethanol and acetic acid in a flow-through mode. A residence time of 20 s gave a

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