Preparation and characterization of Polyvinyl Guanidineacetic (PVG) Membrane for Biodiesel Production

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Abstract: Polyvinyl guanidineacetic (PVG) was prepared by the chemical grafting between poly(vinyl alcohol) (PVA) and guanidineacetic acid. The results showed that the guanidineacetic groups were successfully introduced into the polyvinyl alcohol by fourier transform infrared (FTIR) and thermogravimetry (TG). The effects of the amount of catalyst and reaction time on the PVG grafting rate were investigated. The PVG/NWF composite membrane as a heterogeneous catalyst for biodiesel production was successfully prepared by the solvent phase inversion. The effects of mass ratio of methanol/soybean oil and reaction temperature on the conversions using the composite membrane for transesterification were studied. And the reusability of the composite membrane and the kinetics of the reaction catalyzed by the composite membrane were also investigated. The conversions obtained from the model are in good agreement with the experimental data.

Keywords: PVG (polyvinyl Guanidineacetic); PVA(polyvinyl alcohol); guanidineacetic groups; Biodiesel; transesterification

1. Introduction

Biodiesel is a candidate alternative fossil fuel which has received considerable attention in recent years because it is biodegrable, renewable, and nontoxic [1, 2]. Biodiesel is generally known as alkyl esters of long chain fatty acid which can be produced via transesterification of triglyceride with alcohol (primarily methanol) catalyzed by chemical catalysts, including homogeneous catalysts (e.g. NaOH, KOH) and heterogeneous catalysts (BaO, MgO/SiO_2 and SrO/SiO_2) [3-5]. But new problems arose, such as catalyzers difficult separation from the reaction medium and serious environmental and being not reused [6-8]. 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 [9, 10]. Casimiro et al. [11] prepared PVA supported catalytic membrane synthesized by mutual γ-irradiation method using adipic acid and succinic acid as crosslinkers and a commercial ion exchange resin as catalyst. The catalytic membrane was tested as the potential catalyst under batch conditions in esterification reaction of lauric acid to methyl laurate for biodiesel production. Gao et al. [12] introduce an alkali KF/Ca-Mg-Al hydrotalcite catalyst within a ceramic membrane, using as a heterogeneous to catalyze the transesterification reaction. The conversion of 97.4% within 1 hour was achieved. In our previous work, a blend membrane of sulfonated polyethersulfone (SPES) and PES was employed as an acid catalyst for biodiesel production from free fatty acid. A conversion of over 98% was kept within continuous running time of over 500 h [13].

The aim of the present study is to prepare guanidinylated PVA (PVG) as a heterogeneous alkaline catalyst for the transesterification of soybean oil with methanol. The structure and properties of PVG were studied. 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. The kinetic model for the membrane catalyst in a membrane reactor was developed to predict the catalytic behavior of membrane catalyst as a function of membrane porosity, membrane thickness and internal diffusive resistance of membrane. 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.

2. Materials and Methods

2.1. Materials

PVA with a polymerization degree of 1750±50 was purchased from Beijing Hongxing Chemical Industry, China. Guanidine acetic acid, 4A zeolites, dimethylformamide (DMF), sodium hydroxide (NaOH) and methanol were purchased from Tianjin Kermel Chemical Reagents Limited Company (China). The chemicals were all analytic reagent (AR) grade and used without further purification.

2.2 Preparation of PVG

4.4 g (0.1 mol) PVA, guanidine acetic acid, 250 ml DMF and 4A zeolites were put into a 500 mL three-necked flask and kept at 363K. After the reaction, the mixture was poured into acetone and washed repeatedly with acetone. DMF, unreacted guanidine acetic acid and 4A zeolites were removed, and then dried in oven at 333K.

Finally, the product was soaked with 1mol/L NaOH solution for 24h. And the product PVG was obtained. The synthetic route of PVG was shown in Fig. 1.

(Insert Fig.1 here)

2.3 Preparation of PVG/NWF composite membrane

PVG with a certain weight rate was firstly dissolved in DMF as a solvent by stirring to form a homogeneous PVG solution with a concentration of 10wt.%. Then the NWF was immersed into the PVG solution for 2h. Finally, the PVG/NWF was immediately put into the acetone coagulation baths for preparing the PVG/NWF composite membrane.

2.4. Membrane characterization

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker TENSOR 37 spectrometer, which were collected in the wave number range of 4000–400 cm^{-1} at room temperature. A thermogravimetric (TG) analyzer (Mettler Toledo TGA/SDTA851e, Netzsch company, Germany) was used to test the thermal stability of PVA and PVG. The samples were heated from 25 to 600 °C at a heating rate of 10 °C/min.

The acid capacity [mmol (H^+)/g] of the PVG/NWF composite membrane was determined by an acid-base titration method [15]. The membrane samples were immersed in sodium chloride aqueous solution (0.1 $mol{\cdot}L^{-1}$) to equilibrate for 24 h. Then the ion-exchanged solution was titrated with 0.1 $mol{\cdot}L^{-1}$ potassium hydroxide (KOH) solution using phenolphthalein as an indicator. The acid capacity value (Q) of the membranes was calculated using Eq. (1):

$$Q = \frac{C \times \Delta V}{M} \quad \text{Eq. (1)}$$

where C is the concentration of KOH (mol·L^{-1}), ΔV is the volume of KOH consumed (ml), M is the weight of the dry membrane (g).

The acid amount of the catalytic membrane is the amount of mole of hydrogen ions in the membrane, mmol (H^+). It is the product of acid value and weight of the dry membrane.

The NWF thickness of 1.140 mm was used to prepare PVG/NWF composite membrane. And the PVG composite membrane was measured by screw micrometer (Wuxi Xi Gong Measuring Limited Company of China).

2.5. Continuous transesterificaion in the membrane reactor

The experimental setup of the membrane reactor is as follows: the PVG/NWF composite membrane was cut into round sheet with membrane area 36.3×10^{-4} m^2 and fixed into the reactor. And the reactants containing soybean oil and methanol were pumped into the membrane reactor from the upper inlet, flowed through the PVG/NWF composite membrane to react at 338K and then biodiesel collected at the outlet.

The fatty acid methyl esters (FAME) conversion was determined by ^{1}H NMR [16]. Samples prepared in $CDCl_3$ were recorded on a DRX-500 spectrometer operating at 300 MHz (Bruck Co.). The percent conversion was calculated by the ratio of the area of the singlet peak associated with methyl esters at 3.7 ppm and the peaks at 2.3 ppm representative of the α-methylene protons in the ester molecule. The equation is given in Eq. (2):

$$C = \frac{2ACH_3}{3ACH_2} \times 100\% \qquad \text{Eq. (2)}$$

where C, FAME conversion of feedstock to the corresponding methyl ester; ACH_3, integration area of the protons of the methyl esters (the strong singlet peak); ACH_2, integration area of the methylene protons. The factors 2 and 3 derive from the fact that the methylene carbon possesses two protons and the alcohol (methanol–derived) carbon has three attached protons.

2.6. Kinetics studies

The transesterification of triolein (TG) follows a three-step reaction. In the first step, TG is converted to diolein (DG) and a methyl ester. And then DG is converted to monoolein (MG) and a methyl ester in the second step. In the third step, MG is converted to glycerol and a methyl ester. In each step, one molecule of methyl ester is formed for every molecule of glyceride reacted [17].

The reverse reaction is neglected due to the high methanol concentration. DG and MG concentrations of product are small and can be assumed to be negligible during the course of reaction. Under the above conditions, the reaction rate of the transesterification for forward reaction can be expressed by Eq. (3) [18]:

$$-\mathrm{r}_A = \frac{-d[TG]}{dt} = k' \cdot [TG] \cdot [ROH]^3 \qquad \text{Eq. (3)}$$

where $-r_A$ is the reaction rate of *[TG]* ($\mathrm{mol \cdot cm^{-1} \cdot min^{-1}}$), *[TG]* is the concentration of triglycerides ($\mathrm{mol \cdot cm^{-1}}$) and *[ROH]* that of methanol ($\mathrm{mol \cdot cm^{-1}}$) at the reaction time of t and k is the equilibrium rate constant ($\mathrm{mol^{-3} \cdot cm^{3} \cdot min^{-1}}$).

Because of the high molar ratio of methanol to oil, the change in methanol concentration can be considered as constant during reaction. Hence, the reaction is considered as a first order chemical reaction. Finally, the rate expression can be written as:

$$-\mathrm{r}_A = \frac{-d\left[TG\right]}{dt} = k' \cdot \left[TG\right] \qquad \text{Eq. (4)}$$

where k is modified rate constant (min^{-1}) and $k' = k \cdot [\mathrm{ROH}]^3$.

(Insert Fig.2 here)

Fig. 2 is shown the diffusion mechanism of reactants and products in the membrane. The reactant A was continuously reacting with the molar flow rate F_{A0}. Let us set “M” as any point in the catalytic membrane. The volume of “M” point is dV_t and V_t is the reaction volume. The so-called reaction volume refers to the space of chemical reaction. Because the dV_t is very small, it can be considered as uniform in the reaction system. The reactant A its molar flow rate is F_{A0}, and after reaction the parameter becomes F_{A0}-dF_{A0}. Therefore, the conversion of the reactants in the unit volume per hour, the reaction rate is

$$-\mathrm{r}_A = \frac{-d\left[TG\right]}{dt} = k' \cdot \left[TG\right] \qquad \text{Eq. (5)}$$

Combining Eq. (4) and Eq. (5) can be obtained.

$$-\frac{dF_A}{dV} = -kC_A = -kC_{A_0}(1-x) \qquad \text{Eq. (6)}$$

X and C_{A0} refer to the conversion and the initial concentration of TG.

$$dF_A = kC_{A_0}(1-x)dV \qquad \text{Eq. (7)}$$

Eq. (7) can be converted to Eq. (8)

$$dF_{A_0}(1-x) = kC_{A_0}(1-x)dV \qquad \text{Eq. (8)}$$

Eq. (6) could be expressed as

$$-F_{A_0}dx = kC_{A_0}(1-x)\varepsilon S_m dL \qquad \text{Eq. (9)}$$

where L is membrane thickness (mm); ε is membrane porosity and S_m is reaction area of the catalytic membrane. Eq. (9) can be converted to Eq. (10)

$$-Rdx = k\varepsilon S_m(1-x)dL \qquad \text{Eq. (10)}$$

where R is the flow rate (ml·min^{-1})

$$dx = -\frac{k\varepsilon S_m(1-x)}{R}dL \qquad \text{Eq. (11)}$$

$$-\frac{1}{1-x}dx = \eta_0 \cdot \frac{k\varepsilon S_m}{R}dL \qquad \text{Eq. (12)}$$

η_0, is the internal diffusion efficiency.

Eq. (12) can be converted to Eq. (13)

$$-\ln(1-x)\Big|_{x_{n-1}}^{x_n} = \int_0^L \eta_0 \cdot \frac{k\varepsilon S_m}{R}dL = \eta_0 \cdot \frac{k\varepsilon S_m L}{R} \qquad \text{Eq. (13)}$$

In the multilayer membrane reaction, the first layer of membrane reaction material is

second layers of membrane feed.

$$\ln\frac{1}{1-x_1} = \eta_0 \cdot \frac{k\varepsilon S_m L}{R} \qquad \text{Eq. (14)}$$

$$\ln\frac{1}{1-x_2} - \ln\frac{1}{1-x_1} = \eta_0 \cdot \frac{k\varepsilon S_m L}{R} \qquad \text{Eq. (15)}$$

$$\ln\frac{1}{1-x_3} - \ln\frac{1}{1-x_2} = \eta_0 \cdot \frac{k\varepsilon S_m L}{R} \qquad \text{Eq. (16)}$$

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$$\ln\frac{1}{1-x_n} - \ln\frac{1}{1-x_{n-1}} = \eta_0 \cdot \frac{k\varepsilon S_m L}{R} \qquad \text{Eq. (17)}$$

Superposition：$\ln\dfrac{1}{1-x_n} = \eta_0 \cdot \dfrac{k\varepsilon S_m nL}{R}$ Eq. (18)

If the membrane thickness is different, it can be expressed in Eq. (19)

$$\ln\frac{1}{1-x_n}=\eta_0\cdot\frac{k\varepsilon S_m(L_1+L_2+\cdots+L_n)}{R}\qquad\text{Eq. (19)}$$

If the internal diffusive resistance of membrane is different, it can be expressed in Eq. (20)

$$\ln\frac{1}{1-x_n}=\frac{k\varepsilon S_m(\eta_1 L_1+\eta_2 L_2+\cdots+\eta_n L_n)}{R}\qquad\text{Eq. (20)}$$

If the membrane porosity is different, it can be expressed in Eq. (21)

$$\ln\frac{1}{1-x_n}=\frac{k\varepsilon L(\eta_1 S_{m1}+\eta_2 S_{m2}+\cdots+\eta_n S_{mn})}{R}\qquad\text{Eq. (21)}$$

In the experiment, we found a very interesting phenomenon that the conversion of one layer membrane in N times cycle reaction was different from that of N layers membrane in the reactor.

One layer membrane in N times cycle reaction, Eq. (18) can be expressed as

$$\ln\frac{1}{1-x_n}=\frac{\mathrm{th}L\sqrt{\frac{k\tau}{D_0\varepsilon}}}{\sqrt{\frac{k\tau}{D_0\varepsilon}}}\cdot\frac{k\varepsilon S_m n}{R}\qquad\text{Eq. (22)}$$

η_0 was the internal diffusion coefficient of one layer membrane.

where $\eta_0=\dfrac{\mathrm{th}L\sqrt{\frac{k\tau}{D_0\varepsilon}}}{L\sqrt{\frac{k\tau}{D_0\varepsilon}}}$

D_0 is the diffusion coefficient of solute A in solvent B ($m^2\cdot s^{-1}$). *D_0* can be estimated using the correlation.

$$D_0=D_{AB}=\frac{7.4\times10^{-8}\times(\phi\times M_B)^{0.5}\times T}{\mu\times V_A^{0.6}}\qquad\text{Eq. (23)}$$

where M_B is the molar mass of oleic acid, M_B = 282 $g\cdot mol^{-1}$; μ is the viscosity of oleic acid, μ=25 mPa·s; T is the temperature (K), T = 338.15 K; V_A is the molar volume of methanol, V_A = 42.5 $cm^3 \cdot mol^{-1}$; and φ is the association factor for oleic acid, $\varphi = 1$. As compared with oleic acid molecular, the size of methanol molecular is too small. So it can be considered that methanol molecular as solute A diffused into oleic acid solvent B.

N layers membrane in the reactor, Eq. (18) can be expressed as

$$\ln\frac{1}{1-x_n} = \frac{\mathrm{th} nL\sqrt{\frac{k\tau}{D_0\varepsilon}}}{\sqrt{\frac{k\tau}{D_0\varepsilon}}}\cdot\frac{k\varepsilon S_m}{R} \qquad \text{Eq. (24)}$$

where $\eta_0 = \frac{\mathrm{th} nL\sqrt{\frac{k\tau}{D_0\varepsilon}}}{nL\sqrt{\frac{k\tau}{D_0\varepsilon}}}$

Because the value range of the arcsine hyperbolic function *th* is (-1, 1), the range in Eq.(21) is (0,1). So the case that X in Eq.(20) is larger than that in Eq.(21) and n=1 is excluded. That is to say, the conversion of N times cycle reaction is higher than that of n-sheet membranes reaction in a reactor.

The effect of reaction temperature on the transesterification is listed by Arrhenius equation [19, 20].

$$\mathrm{k} = A\exp\left(-\frac{E_a}{RT}\right) \qquad \text{Eq. (25)}$$

The plots of *lnk* can be used as a function of the reciprocal temperature

$$\mathrm{Ln}k = LnA - \frac{E_a}{RT} \qquad \text{Eq. (26)}$$

Both the pre-exponential factor *A* and the apparent activation energy E_a can be obtained by linear regression.

3. Results and discussion

3.2 FTIR analysis

The FTIR spectra of PVA and PVG are shown in Fig. 3. The FTIR spectra of PVG revealed some new characteristic peaks compared with PVA. The new peak at 1250 cm^{-1} was assigned to the distortion vibration of N-H. Another two significant characteristic peaks for PVG at 1190 cm^{-1} and 1735 cm^{-1} represented the stretching vibration of C-N-C and the stretching vibration of C=N. All of these characteristic peaks suggested that guanidineacetic groups were successfully grafted onto the PVA chains.

(Insert Fig.3 here)

3.2 Thermal analysis

The thermal stabilities of PVA and PVG were investigated by TG as shown in Fig. 4. The maximum weight loss of PVA and PVG appeared at about 240℃ and 120℃ from the TG line, respectively. Nearly 60 wt.% and 80 wt.% of weight loss took place in the range of 120-350℃ due to PVA and PVG decomposition, respectively. Obviously, the thermal stability of PVG is worse than PVA. It indicated that the guanidineacetic groups were grafted onto PVA to destroy the structure of PVA [21]. But the PVG decomposition temperature is far higher than the transesterification. Therefore, it is suitable for PVG to catalyze the transesterification for biodiesel.

(Insert Fig.4 here)

3.3. Effects of synthesis conditions on PVG

The effects of the amount of catalyst and reaction time on the PVG grafting rate were shown in Table 1. It could be seen from Table 1 that the grafting rate initially increased from 5.32% to 10.4% (and the corresponding IEC value from 1.21 to 2.40 mmol/g) with the increasing of the amount of catalyst from 0.5wt% to 2wt%. However, the grafting rate suffered a slight decline when the amount of catalyst increased to 2.5wt%. Therefore, 2wt% amount of catalyst was selected suitably for PVG synthesis.

It also can be found from Table 1 that the grafting rate increased from 4.38% to 10.4% (and the corresponding IEC value from 0.86 to 2.40 mmol/g) with the increase reaction time from 10 h to 16 h. Further increasing reaction time to 16 h, the grafting rate had a slight decline. In sum, the highest grafting rate was obtained at 10.4% and the corresponding maximum IEC value of 2.40 mmol/g for preparation of PVG under the optimal reaction condition of amount of catalyst 2wt% and reaction time of 16 h.

3.4 Catalytic performance of PVG/NWF composite membrane

The effect of temperature on the transesterification is an important for the heterogeneous reaction. The reaction was realized at different temperature of 308, 318, 328, 338, 348 K under methanol/oil mass ratio of 3:1 and the alkali amount of catalytic membrane 18.0 mmol. The effect of temperature on the transesterification was shown in Fig. 5(a). The conversion of soybean oil increased considerably from 74.9% to 98.2% with an increase in temperature from 308 to 338K. But a slight increase in the conversion appears when the temperature was beyond 338K. This is because the evaporation of methanol occurred at above 338K reduced probability of the contact among methanol, oil and catalytic membrane [22]. Therefore, the reaction temperature of 338K was selected.

In order to understand the effect of membrane layers on the catalytic performance and mass transfer resistance, a single to seven layers of membrane were utilized in Fig. 5(b). The reaction conditions were reaction temperature of 338K and the alkali amount of 18.0 mmol. It was found from the Fig. 5(b) that FAME conversion was increased from 74.5% to 98.2% with an increase in the methanol/soybean oil mass ratio from 1:1 to 3:1. Further increasing the ratio from 3:1 to 5:1, the conversion dropped from 98.2% to 98.0%. A low conversion obtained at low methanol/soybean oil mass ratio was due to the incomplete reaction. However, too high methanol/soybean oil mass ratio also leads to a low conversion as a result of the diluted soybean oil concentration in the reaction system [23].

(Insert Fig.5 here)

3.5 Reusability of PVG/NWF composite membrane

The reusability of PVG/NWF composite membrane was investigated under the reaction temperature of 338K, methanol/oil mass ratio of 3:1 and the alkali amount of catalytic membrane 18.0 mmol. The experiments were repeatedly carried out for five runs for 24 h at a time. The conversions for the five runs were 98.2%, 97.6%, 97.2%, 96.5% and 96.1%, respectively. The conversion declined only 2.1% after five runs. The PVG/NWF composite membrane showed excellent catalytic performance and reusability.

3.6 Activation energy and pre-exponential factor

The kinetics experiment of the transesterification of soybean oil and methanol was carried out at the temperature of 308, 318, 328 and 338 K under the reaction conditions of methanol/oil mass ratio of 3:1, reaction temperature of 338K and reaction time of 120 min. The relationship between $-ln(1-X)$ (X stands for FAME conversion) and the reaction time t at different reaction temperatures was investigated. The result showed a linear relationship between $-ln(1-X)$ and t. It was consistent with Eq. (2), which illustrates that the transesterification complied with the first-order reaction. The reaction rate constant k can be obtained from the slope of each straight line as shown in Table 2. The reaction rate constants k increased with an increase in reaction temperature.

Pre-exponential factor A and the apparent activation energy E_a were calculated taking into account the process parameters at different temperatures. As listed in Table 2, two parameters lnk and $1/T$ were analyzed by linear regression. An equation of the straight line (y=11.2382–4885x) was obtained by Origin Software to describe Eq. (4) with a high goodness of Fit (R^2) of 0.995. The apparent activation energy E_a of 40.614 kJ/mol and pre-exponential factor A of 7.60×10^4 were obtained from the Eq. (4). It implies that the reactions are not diffusively controlled but kinetically controlled owning to the high activation energy [24].

Substituting activation energy E_a of 40.614 kJ/mol and pre-exponential factor A of 7.60×10^4 into Eq. (25), Eq. (25) can be expressed as follows:

$$\mathrm{k} = 76000\exp(-\frac{4.885\times10^{3}}{T}) \qquad \text{Eq. (27)}$$

The rate constant *k* could be determined from the Arrhenius plot as a function of temperature *T*.

3.7 Kinetic model prediction

3.7.1 Reaction temperature

The effect of reaction temperature on the conversion can be predicted from the kinetic model. The reaction conditions were membrane area 36.3×10^{-4} m^{2}, membrane thickness 1.732 mm and flow rate 2 mL·min^{-1}. Substituting all the known parameters into Eq. 22 and Eq. 24, Eq. 28 and Eq. 29 was obtained. Eq. 28 and Eq. 29 were solved as a function of reaction temperature in order to predict the effect of reaction temperature on the conversion of one sheet membrane for ten times cycle reaction and ten sheet membranes reaction in a membrane reactor, respectively. The functional relationship between conversion (x) and reaction temperature is shown in Fig. 6(a).

$$\ln\frac{1}{1-x_n} = \eta_0\cdot\frac{k\varepsilon S_m nL}{R} = (76000\exp(-\frac{4.885\times10^{3}}{T}))\times\frac{10\times1.723\times10^{-3}\times36.3\times10^{-4}\times0.68}{2\times10^{-3}/60} \qquad \text{Eq. (28)}$$

$$\ln\frac{1}{1-x_n} = \frac{\mathrm{th}(10\times1.723\times1.96\times10^{-3})}{1.96\times10^{-3}}\times(76000\exp(-\frac{4.885\times10^{3}}{T}))\times\frac{36.3\times10^{-4}\times0.68}{2\times10^{-3}/60} \qquad \text{Eq. (29)}$$

Fig. 6(a) showed that the functional relationship between conversion and reaction temperature was simulated. The point was the experimental value. The red line was the model value obtained by one time reaction of ten layers of membrane fixed in the membrane reactor, and the black line is the model value obtained by ten times of membrane cycle reaction. It can be seen from Fig. 6(a) that the experimental values correspond well with the theoretical simulation values. The conversion increased with the increase of reaction temperature. It can also be seen from Fig. 6(a) that the conversion obtained by ten cycles of one-layer membrane reaction was higher than that obtained by one-time reaction of ten-layer membrane fixed in the membrane reactor. This result is consistent with that obtained by the theoretical model calculation in Part 2.6.

3.7.2 Membrane thickness

The reaction conditions were membrane area 36.3×10^{-4} m^2, membrane porosity 52% and flow rate 2 mL·min^{-1}. Substituting all the known parameters into Eq. 22 and Eq. 24, Eq. 30 and Eq. 31 was obtained. Eq. 30 and Eq. 31were solved as a function of membrane thickness in order to predict the effect of membrane thickness on the conversion of eight times cycle reaction and eight sheet membranes reaction in a membrane reactor, respectively. The functional relationship between conversion (x) and membrane thickness (L) of catalytic membranes is shown in Fig. 6(b).

$$\ln\frac{1}{1-x_n}=\eta_0\cdot\frac{k\varepsilon S_m nL}{R}=\frac{\mathrm{th}(L\times 1.96\times 10^{-3})}{1.96\times 10^{-3}}\times\frac{0.0607\times 36.3\times 10^{-4}\times 0.52\times 8}{2\times 10^{-3}/60}L \qquad \text{Eq. (30)}$$

$$\ln\frac{1}{1-x_n}=\frac{\mathrm{th}nL\sqrt{\frac{k\tau}{D_0\varepsilon}}}{\sqrt{\frac{k\tau}{D_0\varepsilon}}}\cdot\frac{k\varepsilon S_m}{R}=\frac{\mathrm{th}(8L\times 1.96\times 10^{-3})}{1.96\times 10^{-3}}\times 0.0607\times\frac{36.3\times 10^{-4}\times 0.52}{2\times 10^{-3}/60} \qquad \text{Eq. (31)}$$

Fig. 6(b) showed the functional relationship between conversion and thickness of catalytic membrane is simulated by MATLAB software. The point is the experimental value. It can be seen from Fig. 6(b) that the experimental values correspond well with the theoretical simulation values. When L is less than 1.779mm, there is no internal diffusion, and the reaction conversion increased sharply. With the increase of L, the internal diffusion increases and the conversion increases slowly. It can also be seen from Fig. 6(b) that the conversion of one-layer membrane in eight cycles is higher than that of eight-layer membranes fixed in a membrane reactor in one reaction. This result is consistent with that obtained by the theoretical model calculation in Part 2.6.

3.7.3 Volume flow rate

The reaction conditions were membrane area 36.3×10^{-4} m^2, membrane thickness 1.732 mm, membrane porosity 68% and the rate constant (*k*) 0.0607 s^{-1}. Substituting all the known parameters into Eq. 22 and Eq. 24, Eq. 32 and Eq. 33 was obtained. Eq. 32 and Eq. 33 were solved as a function of volume flow rate in order to predict the effect of volume flow rate on the conversion of seven times cycle reaction and seven sheet membranes reaction in the membrane reactor, respectively. The functional relationship between conversion (x) and volume flow rate (R) of catalytic membranes is shown in Fig. 6(c).

$$\ln\frac{1}{1-x_n}=0.0607\times\frac{1.723\times10^{-3}\times7\times36.3\times10^{-4}\times0.68}{R\times10^{-3}/60} \qquad \text{Eq. (32)}$$

$$\ln\frac{1}{1-x_n}=\frac{\text{th}(7\times1.723\times1.96\times10^{-3})}{1.96\times10^{-3}}\times0.0607\times\frac{36.3\times10^{-4}\times0.68}{\text{R}\times10^{-3}/60} \qquad \text{Eq. (33)}$$

The solid line in Fig. 6(c) simulates the functional relationship between reaction conversion and volume flow rate with the software of matlab. The point is the experimental value. It can be seen that there is a good correspondence between the experimental value and the theoretical simulation value. It can also be seen from Fig.

6(c) that the conversion decreased gradually with the increase of volume flow rate. It can also be seen from the figure that the conversion obtained by one membrane cycle reaction seven times is higher than that obtained by the reaction with seven membranes fixed in a membrane reactor, which is consistent with the result obtained by the theoretical model calculation in Part 2.6.

(Insert Fig.6 here)

4. Conclusion

PVG was prepared by the chemical grafting between PVA and guanidineacetic acid. The FTIR spectrum analysis showed that a new peak appeared at 1250 cm^{-1} which was assigned to the distortion vibration of N-H. The TG analysis indicated that the guanidineacetic groups were grafted onto PVA to destroy the structure of PVA. The maximum grafting rate was 10.4% under the conditions of 2wt% amount of catalyst and reaction time of 16 h. The PVG/NWF composite membranes as heterogeneous catalysts for biodiesel production were successfully prepared. The soybean oil conversion of 98.2% was obtained with composite membranes as the catalysts under the optimum reaction conditions of reaction temperature of 338K, methanol/oil mass ratio of 3:1 and the alkali amount of catalytic membrane 18.0 mmol. After five runs, the conversion declined only 2.1%. A kinetic model involving membrane thickness, membrane porosity, internal mass transfer resistance and reaction temperature was established to predict the transesterification conversion. The model predicted results were in good agreement with the experimental data.

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Figure Captions:

Fig. 1 The schematic representation of PVG synthesis

Fig. 2 The diffusion mechanism of reactants and products in the membrane

Fig. 3 FTIR spectra of PVA and PVG

Fig. 4 TG curves of PVA and PVG

Fig. 5 The effects of reaction temperature (a) and methanol/soybean oil mass ratio on the conversion by PVG/NWF composite membrane

Fig. 6 The comparison of predicted catalytic behavior with the experimental data at various reaction temperatures (a), membrane thicknesses (b) and flow rates (c)