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Supporting Information

Continuous biodiesel production from acidic oil using a combination of acidic and alkaline composite catalytic membranes in flow-through membrane reactors

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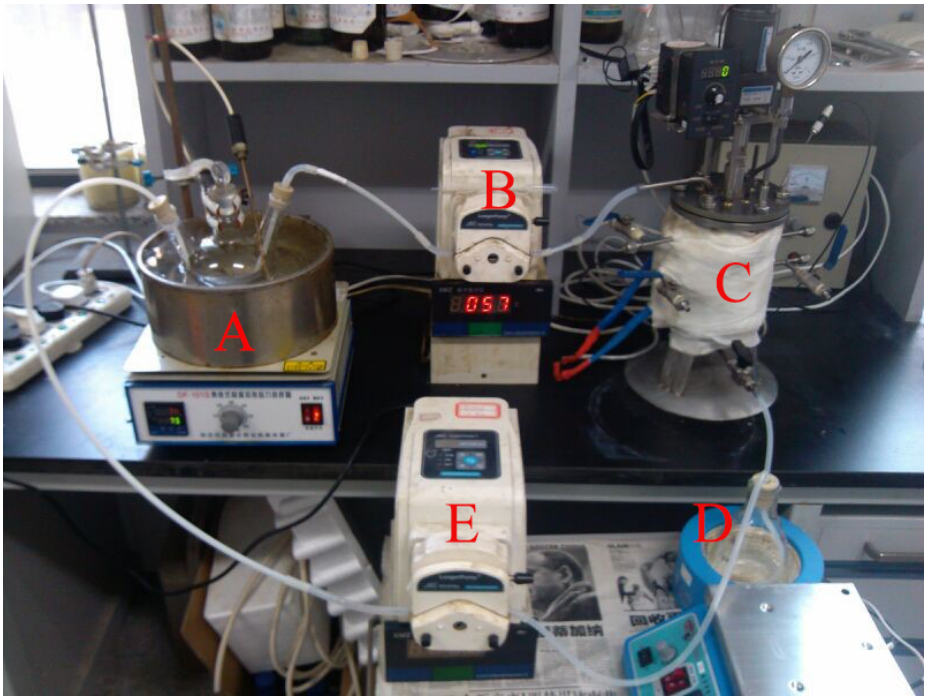

Fig. S1. Physical Flow Chart of Catalytic Reaction

A complete setup diagram on the processes for biodiesel production from acidic oil was shown in Fig. S1. The catalytic membrane reactor (Fig. S1C) was made from stainless steel for acid/alkali resistance. The continuous esterification was carried out in a catalytic membrane reactor. The Acid composite catalytic membranes (ACCMs) were cut into round sheets with a diameter of 68 mm and fixed into the reactor. The catalytic membrane reactor was equipped with a warmer jacket to heat the reactants. Acidic oil and methanol were mixed and preheated in a feedstock tank (Fig. S1A) and then fed to the esterification reactor using a peristaltic pump (Fig. S1B) to esterify. The reactants containing methanol and acidic oil, which flowed through the ACCMs with a mass ratio (methanol and acidic oil) of 3:1, reaction temperature 65 ^{o}C and a volumetric flow rate of 0.2~3 ml min^{-1}. The obtained esterification product mixture from the esterification reactor was introduced into tank (Fig. S1D) to settle for about 30 min, and the mixture was naturally separated into two layers. The upper layer mainly containing methanol, water produced and residual oleic acid with a small amount of biodiesel and soybean oil. Moreover, the bottom layer mainly containing soybean oil and biodiesel, which was named transesterification feedstock, was pumped (Fig. S1E) into the feedstock tank (Fig. S1A).

The polymer-based alkaline composite catalytic membranes (PACCMs) of 3.5 mm thickness was cut into round sheet with a diameter of 68 mm and fixed into the reactor (Fig. S1C). The amount of newly added methanol was added according to the molar

ratio of 9:1 with soybean oil in the product after online separation. The mixed reactant (Fig. S1A) was pumped (Fig. S1B) into the membrane reactor from the upper inlet and flowed through the PACCMs at reaction temperature 60 ℃ and a volumetric flow rate of 1 ml min^{-1}. Finally, the effluent mixture from the reactor was collected into the tank (Fig. S1D). The mixture in the tank was evaporated (Fig. S3) to remove residual methanol.

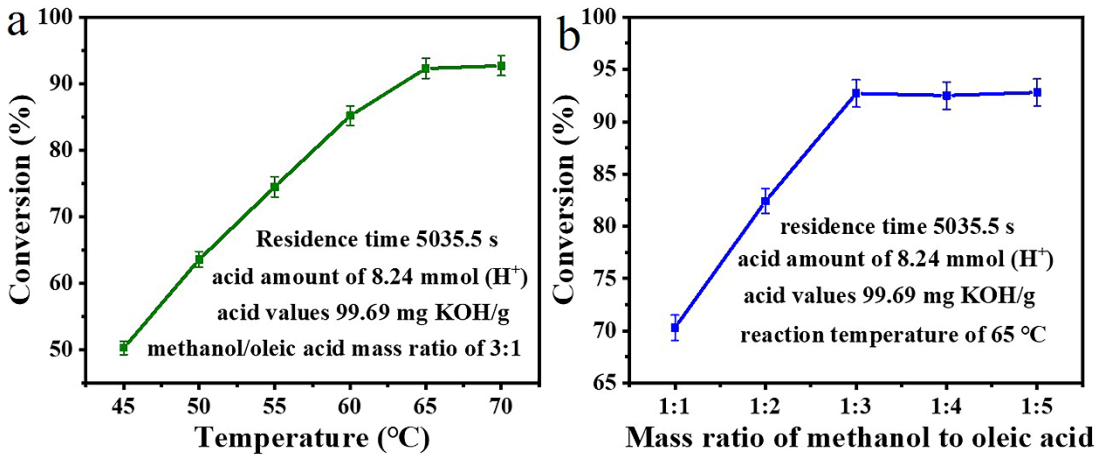

Fig. S2. (a) and (b) Effect of (a) reaction temperature, (b) mass ratio of methanol to oleic acid on the esterification.

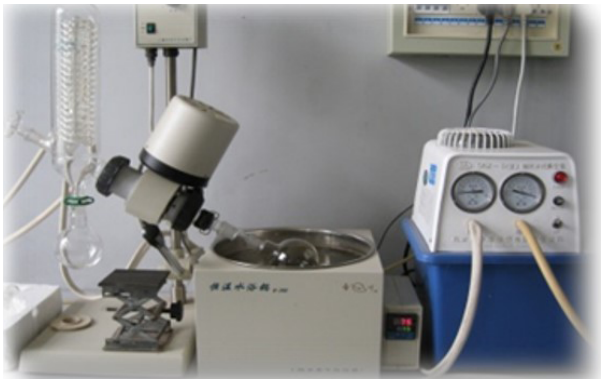

Fig. S3. Rotating distillation equipment

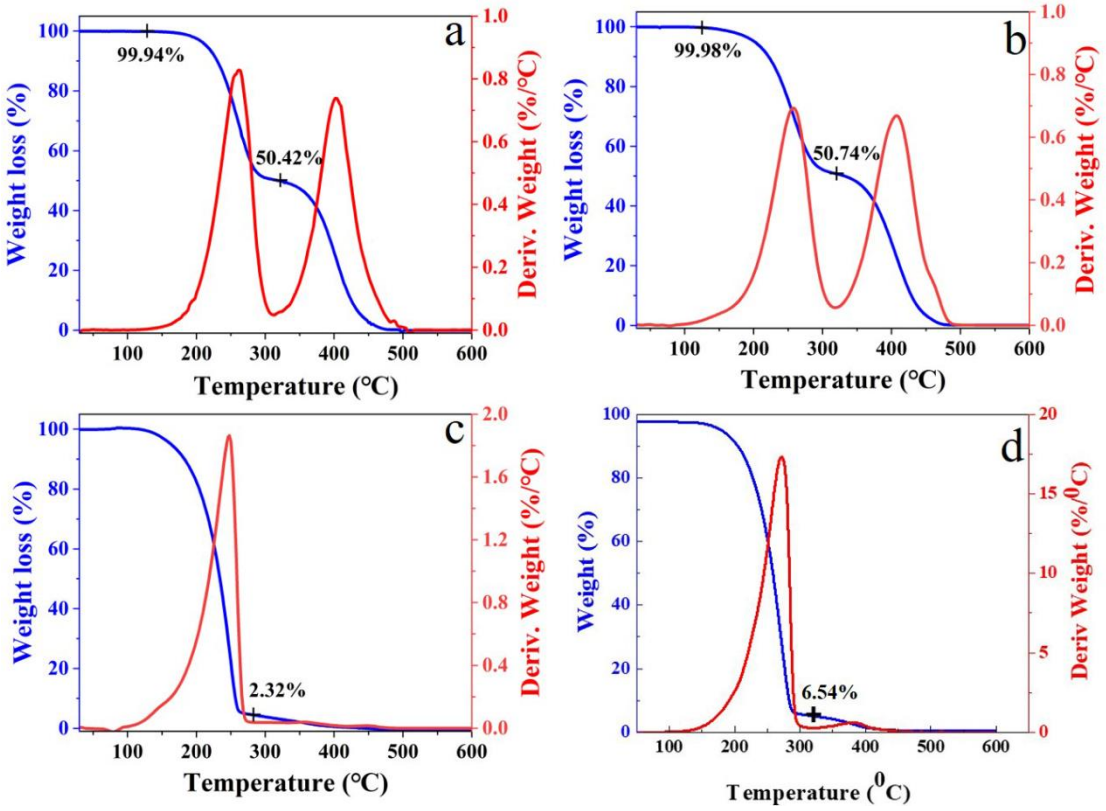

Fig. S4. (a) TG analysis of esterification feedstock. (b) TG analysis of esterification bottom layer products. (c) TG analysis of transesterification products of Route one. (d) TG analysis of transesterification products of Route two.

It can be seen from Fig. S4 that the total mass before and after esterification has almost no change. According to the TG analysis of esterification feed oil in Fig. S4a, 49.52% of the first mass loss is Free fatty acid (FFA) burning loss, and 50.42% of the second mass loss is triglyceride burning loss. According to the TG analysis of the lower layer of esterification products in Fig. S4b, 49.24% of the first mass loss is methyl oleate burning loss, and 50.74% of the second mass loss is triglyceride burning loss. Transesterification stage: the molecular weight of methyl oleate is far less than that of triglyceride, so the calcination temperature of methyl ester and triglyceride can be separated. Therefore, the amount of triglyceride before and after the transesterification reaction can be calculated according to TG [1]. The esterification product is used as the raw material of the transesterification reaction to continue the transesterification reaction. It can be seen from Fig. S4c that the content of triglycerides in the

transesterification products decreased from 50.74% to 2.32%. Through calculation, the conversion rate of triglyceride to methyl ester in the transesterification reaction of route one is 95.43%, that is, the conversion rate of FAME is 95.43%. Similarly, the triglyceride content in Figure 4 decreased from 50.74% to 6.54%. It is calculated that the conversion rate of FAME in route two is 87.11%.

Table S1 Composition analysis of Feedstock oil and esterification products.

Main components	Feedstock oil	Esterification products	
Triglyceride content (wt.%)	50.42	50.74	
		Upper layer	Bottom layer
FFA content (wt.%)	49.62	1.46	0.56
Water content (wt.%)	0.072	1.28	0.21

Table S2 Comparison of product content of the two reaction routes.

Components	Products of route one	Products of route two
FFA content (wt.%)	0.13	0.72
Water content (wt.%)	0.03	0.56
Triglyceride content (wt.%)	2.32	6.54

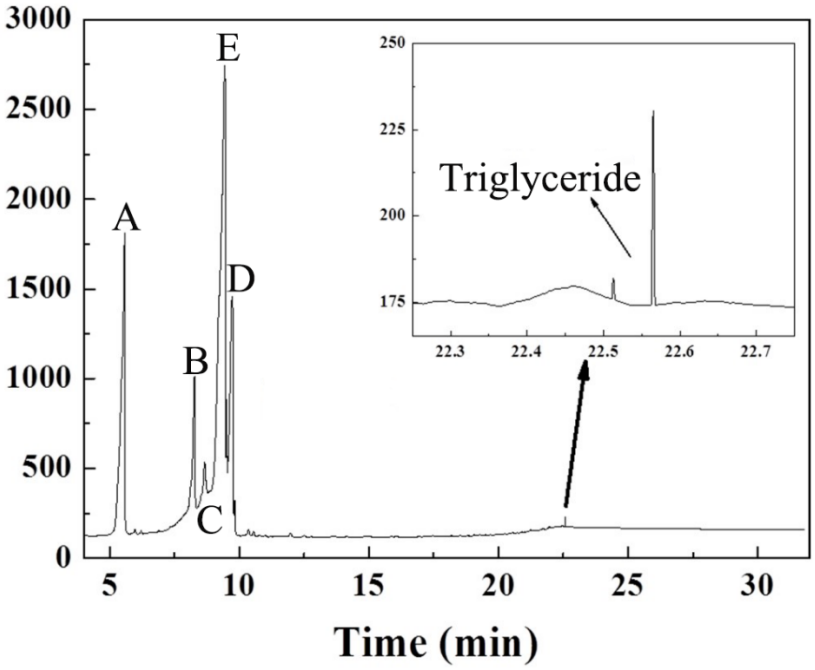

Fig. S5. Gas chromatography of biodiesel

Gas chromatographic conditions:[2] injection port temperature: 250 ℃; Split ratio: 80:1; Injection volume: 1 μ L; Column flow (He): 1.5 mL/min, constant flow mode; FID temperature: 400 ℃; H_2 flow: 40 mL/min; Air flow: 400 mL/min; Make up gas (N_2): 40 mL/min; Furnace temperature program: 210 ℃ for 9 min, and 230 ℃ for 30 min at the rate of 20 ℃/min; Analytical column: 30 m × 320 mm × 0.25 μm HP-INNOWax; Calibration standard sample: heptane solution of methyl dodecanoic (10 mg/mL).

The GC spectra of biodiesel were added in the supplementary information. 250 mg of biodiesel should be weighed, dissolved in 5 ml of methyl dodecanoate, and prepare it into 10 mg/ml internal standard solution for gas chromatography (GC) analysis. The GC analysis results are shown in Fig. 4. Through gas chromatography analysis, there are five major components in biodiesel products. According to the carbon content of methyl ester and the number of unsaturated fatty acid bonds, the product contains five major fatty acid methyl esters, as shown in Figure 4. The five methyl esters are: (A) methyl palmitate, (B) methyl linoleate, (C) methyl oleate, (D) methyl stearate, (E) methyl linoleate. The actual size photos of membrane and reactor equipped with membrane are shown in Fig. 5.

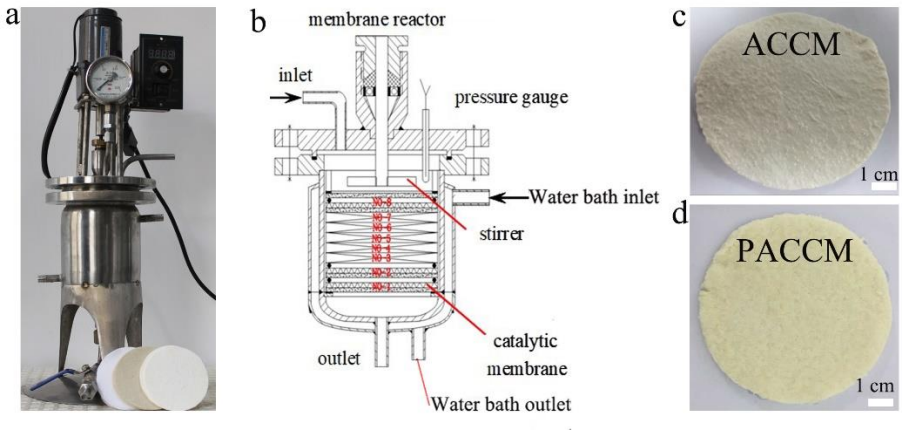

Fig. S6. a) Physical picture of membrane reactor, b) Plan picture of membrane reactor, c) Physical picture of acid composite catalytic membrane (ACCM), and d) Physical picture of polymer based alkaline composite catalytic membrane (PACCM).

Reference

1. J. W. Goodrum, *J. Am. Oil Chem. Soc.*, 1997, **74**, 947-950.
2. 19. G. Knothe, 2001, **44**, 193.