

1 Electronic Supplementary Information:
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3 **Esterification of Fatty Acids from Waste Cooking Oil to Biodiesel Over a**
4 **Sulfonated Resin/PVA Composite**
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1 Experimental Section

2 1. Materials

3 PVA with a polymerization degree of 1750 ± 50 was obtained from Tianjin Kermel Chemical Reagents
4 Ltd., China. Sulfonated cation exchange resin (s-CER), NKC-9 in acidic form (average size of 0.83 mm,
5 see Table S1 for more details), was purchased from the Nankai Group. The average particle size of the
6 grounded s-CER analyzed by laser scattering particle analyzer (BT-9300H, Dandong Baite Instrument
7 CO., Ltd. Dandong, China) was $24.96 \mu\text{m}$. FFAs obtained from WCO with an acid value of 152.3 mg
8 KOH g^{-1} was kindly supplied by Hubei Haolin Bioenergy Company and filtered to remove impurities.
9 No water was detected by a Karl Fischer water tester with a sensitivity of 500 ppm (KF-1A, Shanghai
10 Precision and Scientific Instrument Co. Ltd., China). The average molecular weight of the FFAs was 371
11 g mol^{-1} calculated by saponification value. The sources of WCO were broad and the extracted FFAs
12 contained trace sulfur (140 ppm). The main compositions of the FFAs analyzed by a GC-MS (6890N
13 GC/5973 MS, Agilent) were dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecadienoic
14 acid. The detailed information of the FFAs is provided in Table S2. The other chemicals were all
15 analytical reagent (AR) grade and used without further purification.

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17 2. Physical characterization

18 The composite samples were freeze-dried at 213 K in vacuum and then fractured to expose the cross-
19 sectional area in liquid nitrogen. The composite samples for measurement of scanning electron
20 microscope (SEM) were coated by gold via sputtering at 20 mA for 180 s. The cross-section morphology
21 of the composite was inspected under a Zeiss Ultra plus field-emission scanning electron microscope
22 (FESEM) (Zeiss Co.) equipped with an energy dispersive X-ray (EDX) detector operating at an
23 accelerating voltage of 10 kV. The composites annealed at different temperatures were characterized by
24 a TENSOR-37 Fourier transform infrared spectroscopy (FTIR) (Bruker Co.) operated by attenuated total
25 reflectance (ATR) in the wave number range of $4000\text{-}500 \text{ cm}^{-1}$. The thermal stability of the composites
26 was investigated using a STA449 F3 Jupiter (Netzsch Co.). Thermo gravimetric analysis (TGA) was

1 carried out under a nitrogen atmosphere at a heating rate of 10 K min^{-1} from 323 to 773 K. Ion exchange
2 capacity (IEC) indicates the number of milli equivalents of ions (H^+) in dry composite of unit quality.[1]
3 The IEC of the composites was obtained using the KOH titration method. The reported values were the
4 mean of at least five measurements and the average experimental error was $\pm 5\%$. Swelling degree (SD)
5 represents the swelling status of the composite in the solvent and was measured according to Caetano's
6 method.[2] SD was calculated by dividing the initial sample mass by the mass difference between swollen
7 sample and initial sample. The porosity of the composite flake was obtained by dividing the mass
8 difference between dry and water-saturated composite by area and thickness according to Ding's
9 method.[3] Sulfur content in the FFAs and biodiesel were tested by a micro-coulometry analyzer (WK-
10 2D, Jianfen Electrochemical Instrument CO., LTD. China) and water content was detected by a Karl
11 Fischer water tester. The elemental composition of the samples was studied by elemental analysis with a
12 Perkin-Elmer 2400 Series II CHNS/O analyzer (PerkinElmer Co.). Analyses of FFAs and FAME were
13 performed on a GC (7890B, Agilent) equipped with a HP-5 column. The temperatures of the injector and
14 FID detector were both at 523 K. The oven temperature was ramped from 333 K to 513 K at a rate of 10
15 K min^{-1} and held at 513 K for 10 min.

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17 **3. Esterification catalyzed by s-CER/PVA**

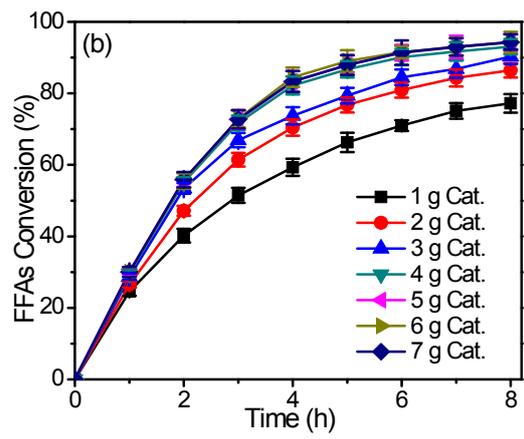
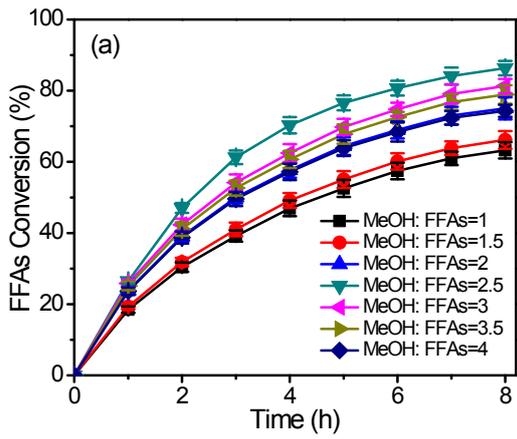
18 For the esterification reaction, the composite flakes were cut into small pieces (about $0.5 \text{ cm} \times 0.5 \text{ cm}$) to
19 achieve better contact with the reactants and to remove the influence of diffusion on esterification. The
20 FFAs were first introduced into the reactor and heated to the desired temperature. Then the desired amount
21 of the methanol and the composite flakes were added into the reactor and the reaction began at pre-
22 determined conditions. The samples were taken out from the reactor every hour and treated by
23 decompression distillation to remove unreacted methanol and water produced to determine acid value and
24 FFAs conversion. After completion, the reaction mixture was poured into a separating funnel and allowed
25 to settle for 1 h to separate the excess methanol and the biodiesel. The biodiesel was further purified by
26 decompression distillation to remove excess methanol and other impurities. The compositions of the

1 biodiesel were analyzed by GC (7890B, Agilent) and listed in Table S4. In reusability experiments, the
2 composites were reused in the next run without further treatment.

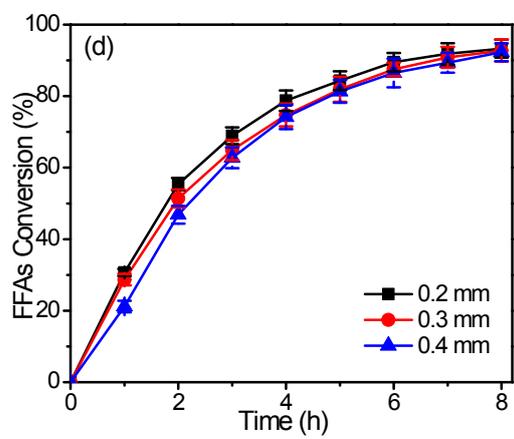
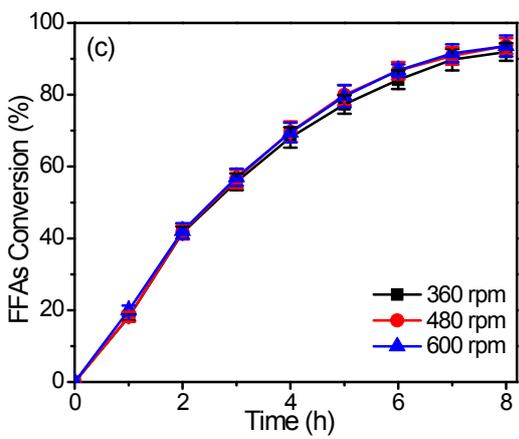
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4 The optimal reaction conditions were comprehensively studied and the results are listed in Fig. S1. As an
5 example, the FFAs conversion increased from 63.2% to 86.3 % with the increase of methanol/FFAs mass
6 ratio from 0.5: 1 to 2.5: 1 (Fig. S1(a)). However, the FFAs conversion decreased to 74.3 % when the mass
7 ratio further increased to 4: 1, which is mainly because the excess methanol would adsorb on the catalytic
8 membrane surface and decrease the catalytic activity or even deactivate the composite. Therefore, the
9 optimal methanol/FFAs mass ratio is 2.5: 1 in the reaction system.

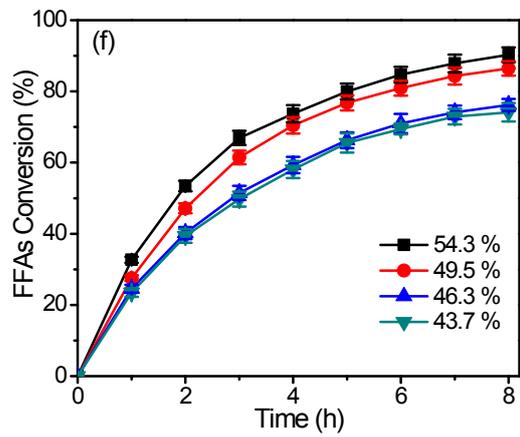
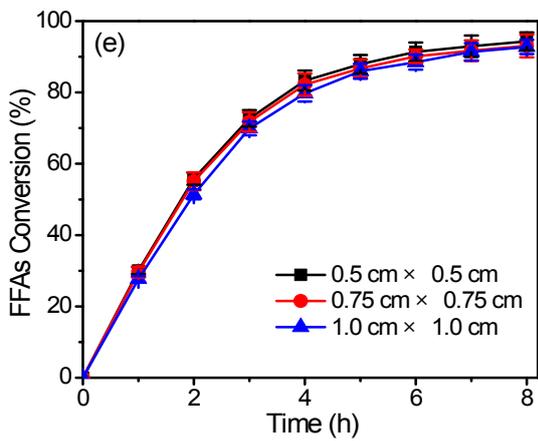
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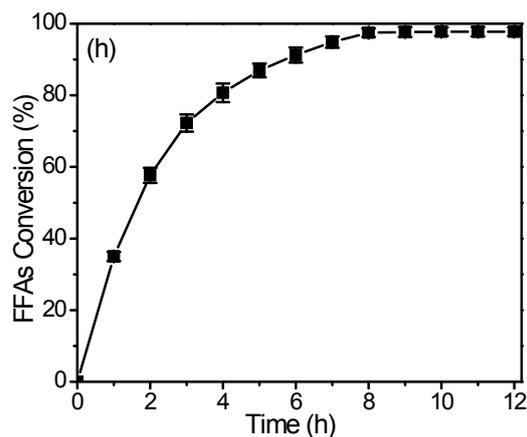
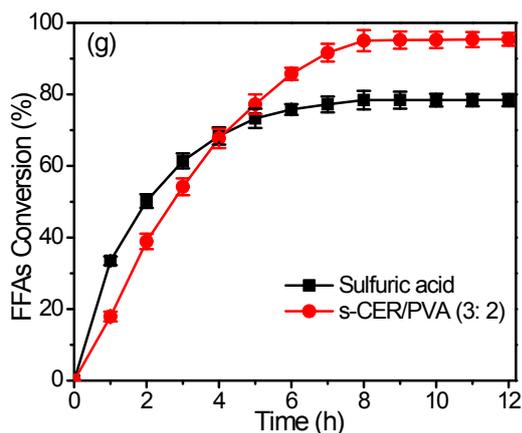
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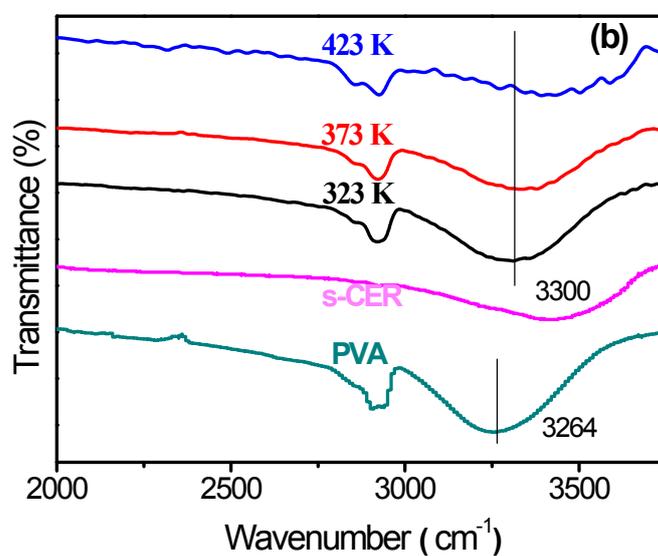
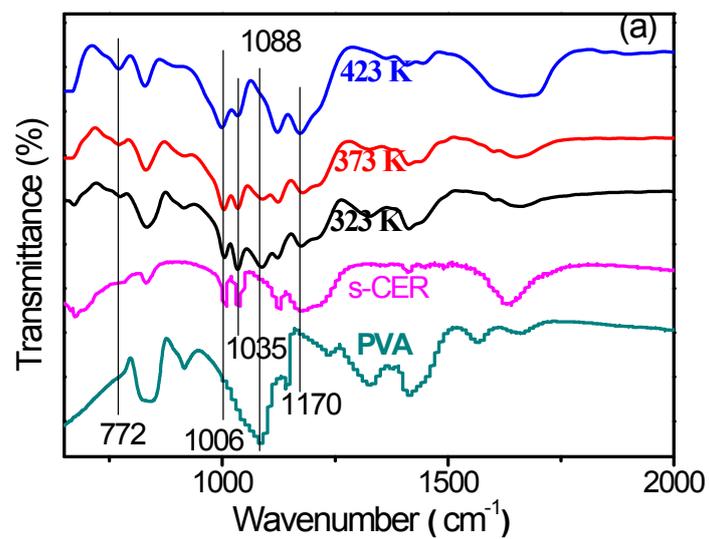


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 2 **Fig. S1.** Esterification of FFAs catalyzed by s-CER/PVA (mass ratio =3: 2) under different reaction
 3 conditions. The results were used to optimize reaction conditions. (a) Effect of methanol: FFAs mass
 4 ratio; (b) Effect of catalyst loading; (c) Effect of mechanical stirring rate; (d) Effect of catalyst thickness;
 5 (e) Effect of catalyst dimension; (f) Effect of catalyst porosity (the different porosities of catalysts were
 6 obtained using different ethanol/water ratio during phase inversion); (g) Effect of reaction time (the
 7 equilibrium time for esterification was 8 h); and (h) the equilibrium conversion under the optimal reaction
 8 conditions according to results from (a)-(g).

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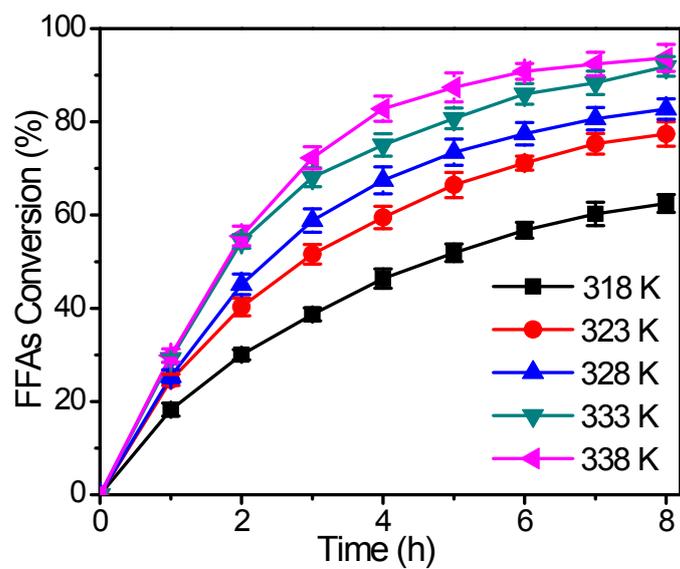
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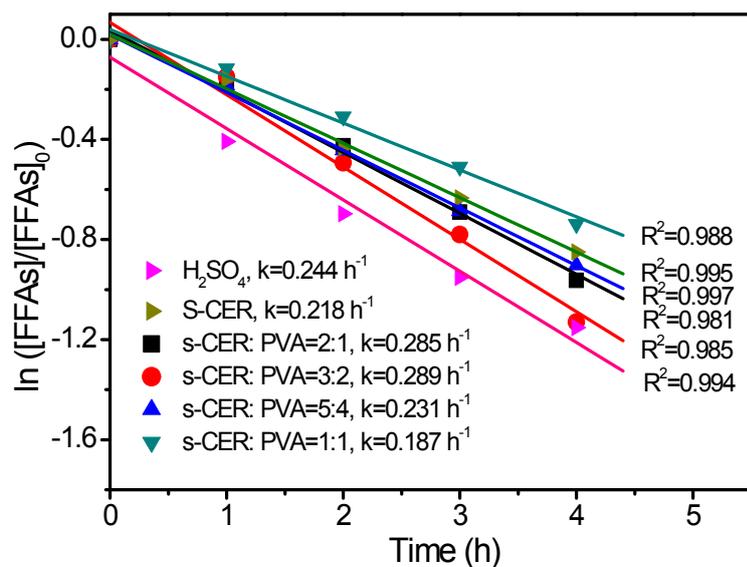
6 **Fig. S2.** FTIR spectra of PVA, s-CER and s-CER/PVA composites (mass ratio 3: 2) annealed at 323,
7 373 and 423 K at wavenumber of 650-2000 cm^{-1} (a) and 2000-3750 cm^{-1} (b).

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2 **Fig. S3.** Effect of reaction temperature on esterification (Reaction conditions: FFAs 20 g, methanol 50
3 g, catalyst loading 4 g and mechanical stirring rate 480 rpm).

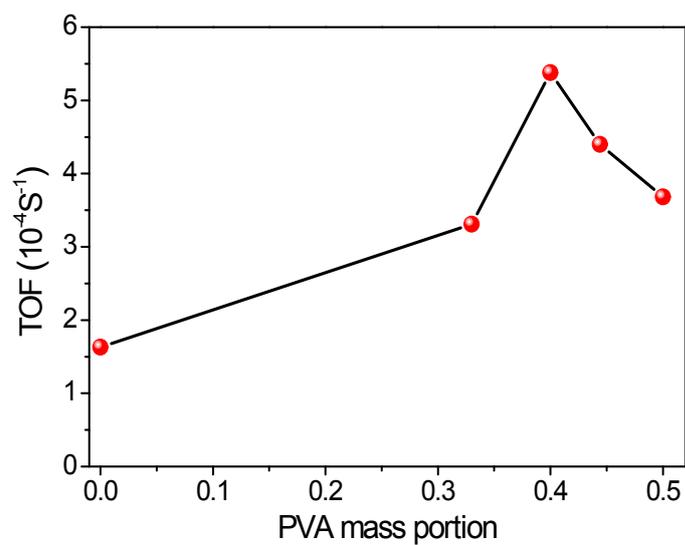
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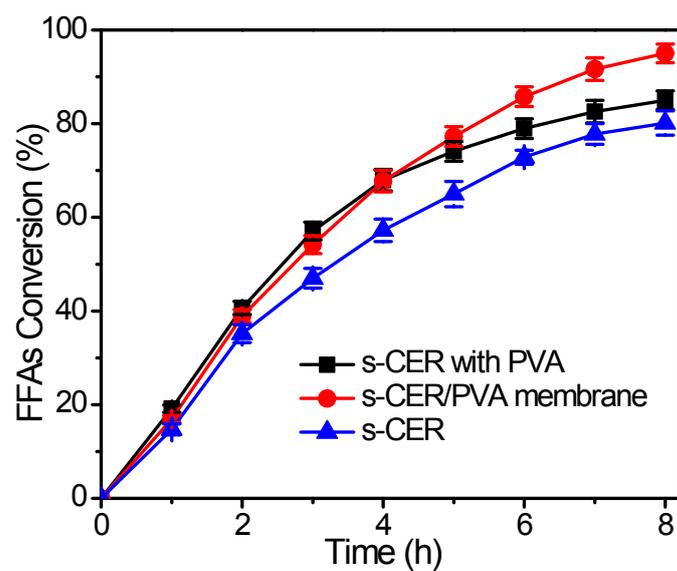
3 **Fig. S4.** Linear relationships between $\ln([FFAs]/[FFAs]_0)$ and reaction time t for esterification
 4 reactions catalyzed by ground s-CER, PVA, s-CER/PVA and H_2SO_4 (Reaction conditions: FFAs 20 g,
 5 methanol 50 g, catalyst loading 4 g except H_2SO_4 (1 g, same number of H^+ as 4 g s-CER), reaction
 6 temperature 338 K and stirring rate 480 rpm). The obtained pseudo-first-order reaction rate constants
 7 were used to calculate the TOF number.

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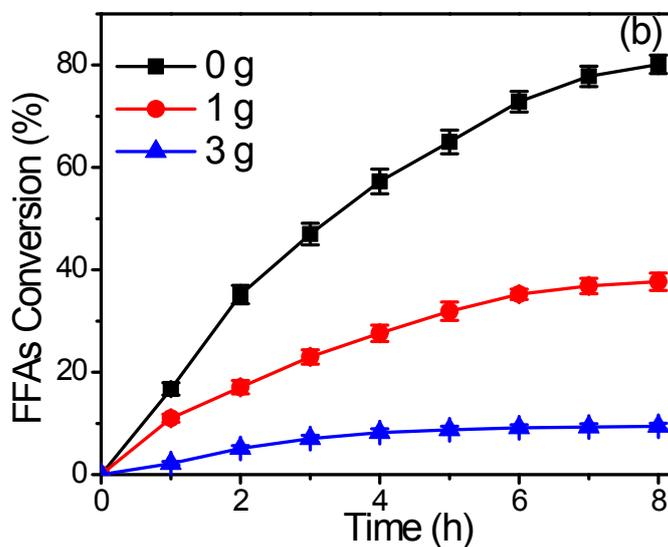
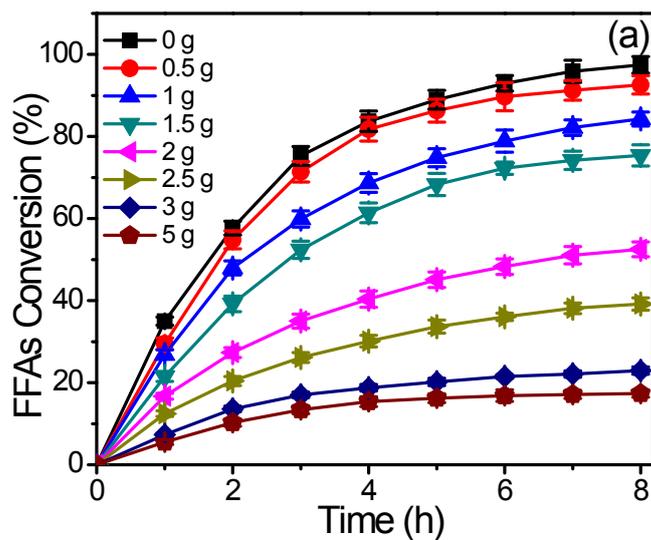
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2 **Fig. S5.** Relationship between mass portion of PVA in catalysts and its corresponding TOF.

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2 Fig. S6. Comparison of esterification catalyzed by “s-CER with PVA”, s-CER/PVA composite and s-
3 CER alone (Reaction conditions: FFAs 20 g, methanol 50 g, catalyst loading 4 g, and mechanical
4 stirring rate 480 rpm). “s-CER with PVA” represents a simple physical mixing of s-CER and PVA.

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3 **Fig. S7.** Effect of water addition on esterification catalyzed by s-CER/PVA (a) and ground s-CER (b).

4 (Reaction conditions: FFAs 20 g, methanol 50 g, s-CER/PVA composite loading 4 g (or ground s-CER

5 with same amount of catalytic sites), and mechanical stirring rate 480 rpm)

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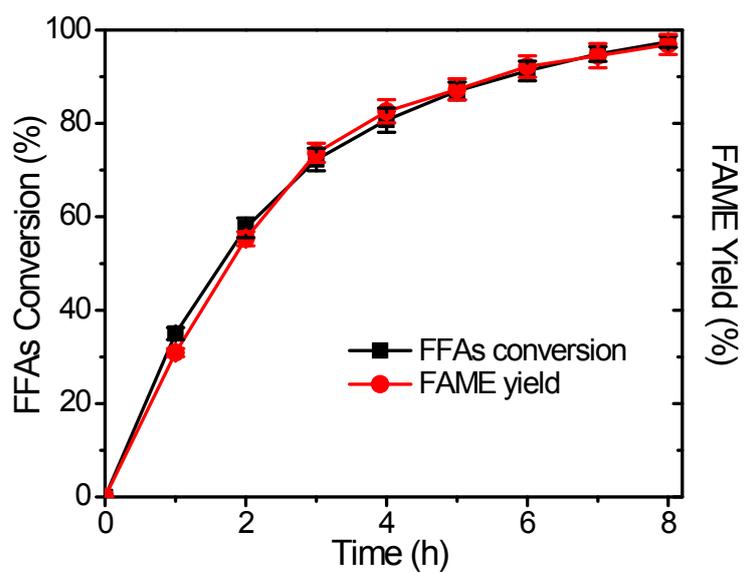
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3 Fig. S8 Comparison of time-dependant FFAs conversion calculated based on KOH titration and GC
4 analyses.

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1 **Table S1** Characteristics of the sulfonated cation exchange resin

Property	NKC-9
Structure	Macroporous structure
Matrix	Styrene, divinyl-benzene
Functional groups	Sulfonated
Form	H ⁺
Total exchange capacity (mmol g ⁻¹ , dry)	≥4.7
Surface area (m ² g ⁻¹)	77
Particles size range (mm)	0.4~1.25
Maximum operating temperature (K)	413
Average pore diameter (nm)	56
Moisture content (%)	≤5
Density True (g ml ⁻¹)	1.20~1.30
Density Apparent (g ml ⁻¹)	0.70~0.80

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3 **Table S2** GC results of the FFAs

Peak	Retention Time (min)	Constituents	Fatty Acid	Mole fraction (%)	
				Before reaction	After reaction ^b
A	13.814	Dodecanoic acid	C12: 0 ^a	17.2	0.6
B	15.441	Myristic acid	C14: 0	4.3	0.1
C	17.289	Palmitic acid	C16: 0	22.7	0.7
D	19.256	Octadecadienoic acid	C18: 2	55.8	1.8

4 ^a: the first number stands for the number of the carbon in the compound; the second number stands for the number
5 of C=C double bond in the compound; ^bUnder optimal reaction conditions.

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7 **Table S3** Effect of ethanol percentages in ethanol/water bath on the porosity of s-CER/PVA (s-CER:
8 PVA mass ratio 3: 2, annealing temperature 373 K)

Ethanol percentages	100 %	80 %	60 %	40 %
Porosity	54.3 %	49.5 %	46.3 %	43.7 %

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11 **Table S4** GC results of the products (Esterification results obtained under optimal reaction conditions;
12 Both the FFAs conversion and the FAME yield were 96.8 % calculated from the GC results)

Peak	Retention Time (min)	Constituents	Fatty Acid	Mole fraction (%)
A	16.132	Methyl Laurate	C12: 0*	16.6
B	17.841	Methyl myristate	C14: 0	4.2
C	19.531	Methyl hexadecanoate	C16: 0	22.0
D	21.091	Methyl linoleate	C18: 2	54.0

1 *: the first number stands for the number of the carbon in the compound; the second number stands for the number
2 of C=C double bond in the compound.

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5 **Table S5** IEC and SD values of ground s-CER, PVA, and s-CER/PVA composite catalysts before and
6 after 6 times' reaction

s-CER: PVA mass ratio	IEC ^a	IEC ^b	IEC ^c	SD ^a	SD ^b	SD ^c
s-CER	5	4.5	5	0.69	0.24	0.69
1: 1	1.9	1.85	1.9	1.46	0.6	1.45
5: 4	1.96	1.9	1.95	1.59	0.64	1.59
3: 2	2.01	1.94	2.01	1.67	0.56	1.66
2: 1	2.75	2.46	2.74	1.73	0.67	1.72
PVA	—	—	—	2.06	0.06	2.05

7 All the catalysts were annealed at 373 K.

8 ^a Newly prepared catalytic catalysts;

9 ^b Catalysts after 6 runs (the catalysts were air dried in a fume hood for 12 h before analysis);

10 ^c Catalysts after 6 runs (the catalysts were first washed with ethyl ether to remove organic components and then
11 washed with ethanol and then dried in a vacuum oven at 373 K for 24 h to remove residual water completely before
12 analysis).

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20 **Table S6** Esterification of single component FFAs and oleic acid in separate batches catalyzed by s-
21 CER/PVA composite (mass ratio 3:2) under typical reaction conditions (FFAs 20 g, methanol 50 g,
22 reaction temperature 338 K, catalyst loading 4 g and mechanical stirring rate 480 rpm)

Entry	Alcohol	FFAs	Products	Yield (%)
1	Methanol	Dodecanoic acid	Methyl Laurate	97.9
2	Methanol	Myristic acid	Methyl myristate	95.8
3	Methanol	Palmitic acid	Methyl hexadecanoate	95.1
4	Methanol	Stearic acid	Methyl stearate	93.4
5	Methanol	Oleic acid	Methyl oleate	93.9

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4 **Table S7** Sulfur content of catalysts with CER/PVA mass ratio of 3: 2 by elemental analysis

Annealling temperatures (K)	Before reaction (wt. %)	After 6 times' reaction (wt. %)
323	7.87	7.82
373	8.32	8.30
423	8.35	8.31

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8 **Table S8** Sulfur content in the reaction solution after each reaction

Reaction cycles	1	2	3	4	5	6
S content before reaction (ppm)	143	143	143	143	143	143
S content after reaction (ppm)	142	143	142	142	143	141

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1 **Note and references**

2 [1] Zhang H, Ding J, Qiu Y, Zhao Z. *Bioresour Technol* 2012;112:28-33.

3 [2] Caetano C S, Guerreiro L, Fonseca I M, Ramos A M, Vital J, Castanheiro J E. *Appl Catal, A*
4 2009;359:41-6.

5 [3] Ding J, He B, Li J. *Journal of Biobased Materials and Bioenergy* 2011;5:1-7.

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