

Supporting information

Highly selective and low-temperature hydrothermal conversion of natural oils to fatty alcohols

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Experimental Section

Chemicals: Unless specifically stated, chemicals used included glucose (99%, Sigma-Aldrich), starch (Weifang fengzheng flour Co.), saw dust (Shenzhen kanuo pet Co.) melamine (99%, Sinopharm), activated carbon (Sigma-Aldrich), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (99.9%, Amethyst), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (99%, Sinopharm), ZnCl_2 (98%, Sinopharm), ZrO_2 (Shanghai maikun Co.), TiO_2 (Shanghai maikun Co.), Al_2O_3 (Shanghai maikun Co.), SiO_2 (Shanghai maikun Co.), algae oil (Beijing Wisapple Biotech Co.), coconut oil (J&K Co), palm oil (J&K Co.), methyl stearate, (J&K Co.), methyl palmitate (J&K Co.), methyl laurate (J&K Co.), stearic acid (Sinopharm chemical reagent Co), lauric acid (98.5%, Cheng Du Mixy chemical Co.), Nitrogen, hydrogen gases and air (99.999 vol. % were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of N-doped carbon support from glucose and melamine: In a typical procedure the nitrogen doped carbon support was synthesized using melamine, glucose and zinc chloride. The weight ratio of glucose to melamine was taken as (1:1). The weight ratio of glucose and zinc chloride was fixed as (1:3). The mixture of these three substances were ground in agate mortar to one hour to mix well and transferred to ceramic boat for calcinations. The calcination was carried out in nitrogen flow at 3.3 °C /min at 800 °C and kept for 1 h. The calcinations furnace was naturally cooled to room temperature and the sample was crushed into powder form in agate mortar. The sample was treated with 3M HCl to remove the zinc chloride thoroughly. The sample was filtered and washed several times using DI water as far as no Cl⁻ ion was detected in supernatant. Finally, the product N-C was dried in an oven at 60 °C and kept for 20 h.

Synthesis of RuSn/N-C via wet impregnation method: The nanoparticles such as Ru and Sn were introduced into the N-C support using wet impregnation method. Nano particles were loaded in Ru (2.5% wt) and (Sn 2.5% wt). After impregnation the samples were dried well in oven. Finally, the samples were reduced under H₂ flow at 350 °C for 4h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C min⁻¹). The samples were named as RuSn/N-C, Ru/N-C, RuSn/C and Ru/C.

Synthesis of RuSn/N-C from saw dust: Certain amount of crushed saw dust was washed well using DI water and dried in an oven. About 4 g of dried saw dust was taken and treated with concentrated sulphuric acid at 60 °C for two hours until the yellow colour turned into black. Then, the black saw dust was thoroughly washed with ultra pre water and dried. The black powder was uniformly mixed with melamine. The mixture was heated to 800 °C in a tube furnace for two hours with a ramping rate of 10 °C min⁻¹. Finally, the product was passed through the wet impregnation method and then reduced the catalyst. The reduction was carried out using H₂ flow at 350 °C for 4 h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C min⁻¹).

Synthesis of RuSn/N-C from starch: The nitrogen doped carbon support was synthesized using starch, melamine and zinc chloride with the weight ratio of (1:1:3). The mixture of these three substances were ground in agate mortar to one hour to mix well and transferred to ceramic boat for calcinations. The calcination was carried out in nitrogen flow at 3.3 °C /min at 800 °C and kept for 1 h. The calcinations furnace was naturally cooled to room temperature and the sample was crushed into powder form in agate mortar. The sample was treated with 3M HCl to remove the zinc chloride thoroughly. The sample was filtered and washed several times using DI water as far as no Cl⁻ ion was detected in supernatant. Finally, the product N-C was dried in an oven at 60 °C and kept for 20 h. The nanoparticles such as Ru and Sn were introduced into the N-C support using wet impregnation method. Nanoparticles were loaded in Ru (2.5% wt) and Sn (2.5% wt).

After impregnation the samples were dried well in oven. Finally, the samples were reduced under H₂ flow at 350 °C for 4h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C min⁻¹).

Synthesis of the RuSn catalysts supported on activated carbon, ZrO₂, TiO₂, SiO₂, and Al₂O₃: The nanoparticles Ru and Sn were introduced into other different supports including activated carbon and other metal oxides such as ZrO₂, TiO₂, SiO₂ and Al₂O₃ via wet impregnation method and then reduced. The samples were reduced using H₂ flow at 350 °C for 4 h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C min⁻¹).

Catalytic characterization

Powder X-ray diffraction (XRD) patterns were detected to investigate the structure and crystal size by Rigaku Ultima IV X-ray diffractometer utilizing Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) operated at 35 kV and 25 mA. N₂ adsorption measurements were performed at 77 K on a BEL-MAX gas/vapor adsorption instrument. The surface areas were determined by the Brunauer-Emmett-Teller (BET) method. The IR spectra of adsorbed butanoic acid (IR-butanoic acid) were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an in-situ IR cell. Scanning electron microscopy images (SEM) were collected by the Hitachi S-4800 microscope. To illuminate crystal morphology and size, transmission electron microscopy (TEM) images were obtained by the FEI Tecnai G2 F30 microscope working at 300 kV. The calcined samples were characterized by temperature-programmed reduction using a TP-5080 adsorption instrument (equipped with a TCD detector). The gas product was a mixed gas of 5% H₂/He, and the heating rate was 5 °C·min⁻¹. The Raman spectra were recorded on a Raman spectrometer of (JY, HR 800) applying a 514-nm laser. X-ray photoelectron spectroscopy (XPS) were carried out with Al K α ($h\nu = 1486.6 \text{ eV}$) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected by using the C 1s peak owing to adventitious carbon with EB fixed at 284.6 eV.

Catalytic tests

In a typical hydrogenation process, 0.1 g catalyst (RuSn/N-C) as described in the manuscript, 0.4 g stearic acid (or 0.4 g oils) and 80 ml DI water were added into micro reactor. The autoclave was purged with N₂ three times to remove the residual air and then introduced reaction gas (5 MPa H₂) at ambient temperature. The reaction was performed in the micro reactor at 140 °C and kept for 6 h with the stirring speed of 500 rpm. The autoclave was cooled to room temperature naturally. After the reaction, diethyl ether was added to the aqueous solvent to extract the products and substrate, and then analyzed by GC-FID and the products were identified by GC-MS.

Test of the natural oil components

Natural oil (5.0 g), methanol (100 mL), and CaO (0.8 g) were added into a micro reactor. The reactor was then flushed with nitrogen at ambient temperature for three times. After evacuating N₂, it was heated up to 80 °C. The reaction was carried out for 2 h at a stirring speed of 600 rpm. After cooling down to ambient temperature, the liquid products were analyzed by GC coupled with GC-MS.

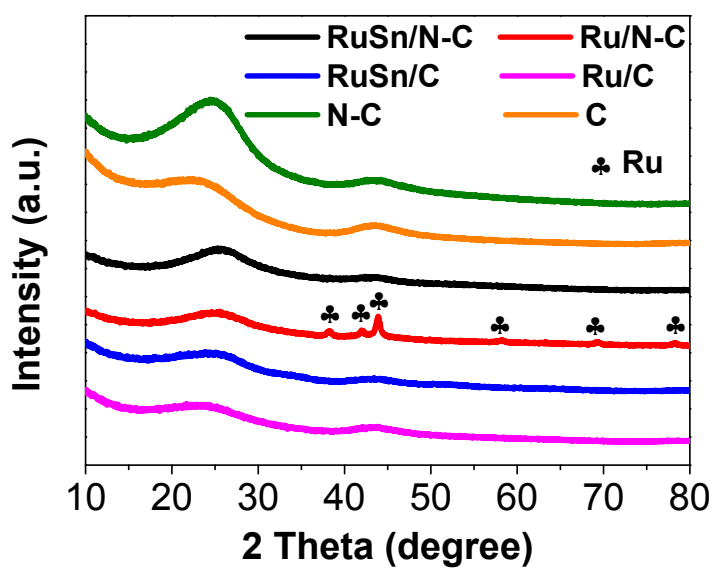


Fig. S1 XRD patterns of the applied samples.

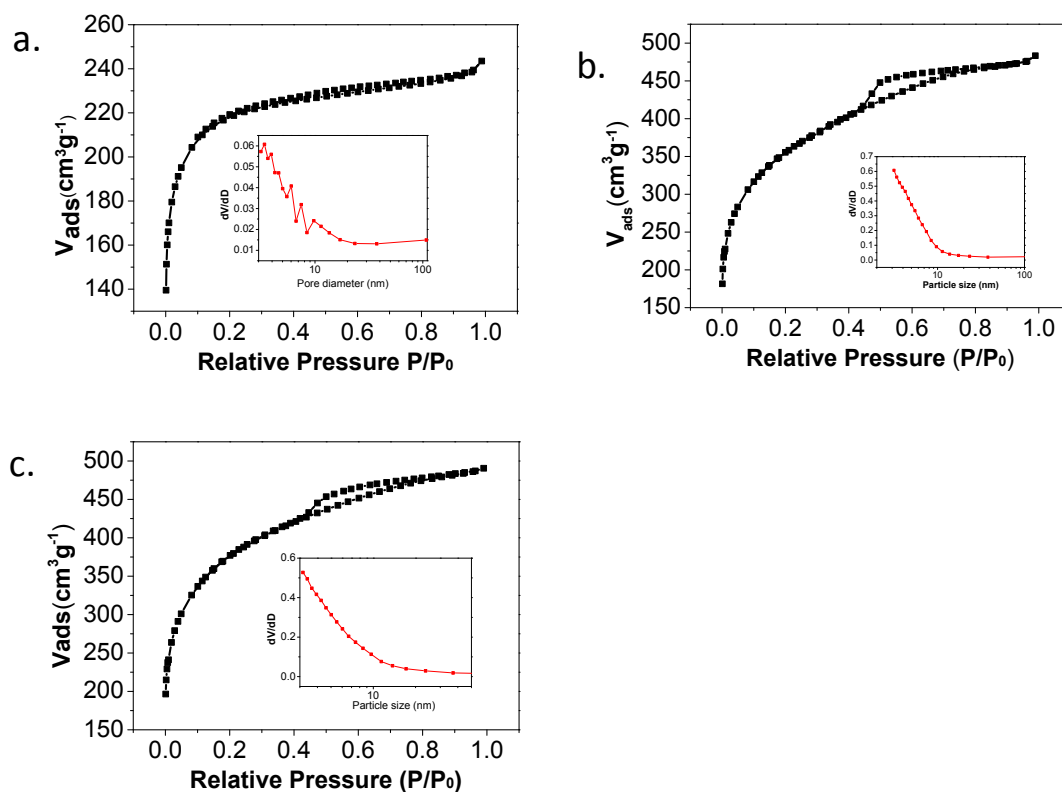


Fig. S2 N₂ adsorption and desorption isotherms of (a) Ru/N-C, (b) RuSn/C and (c) Ru/C catalysts while inset shows their pore size distribution.

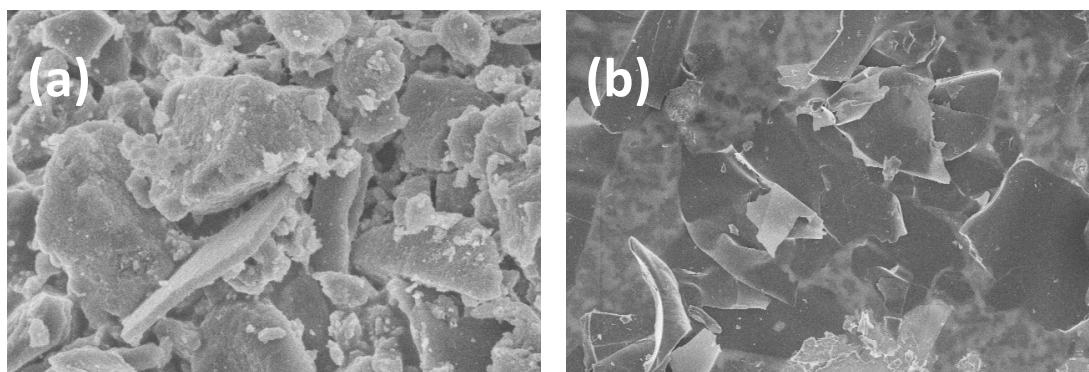


Fig. S3 SEM images of (a) RuSn/C and (b) RuSn/N-C catalysts.

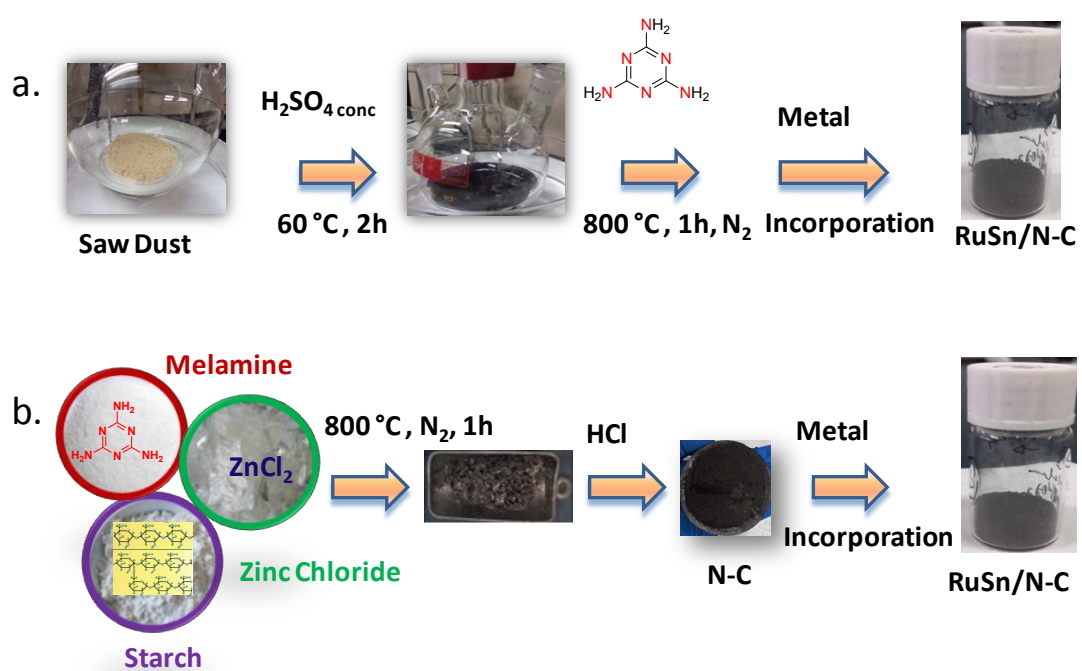


Fig. S4 Schematic diagram for synthesis of RuSn/N-C catalyst from (a) starch and (b) saw dust.

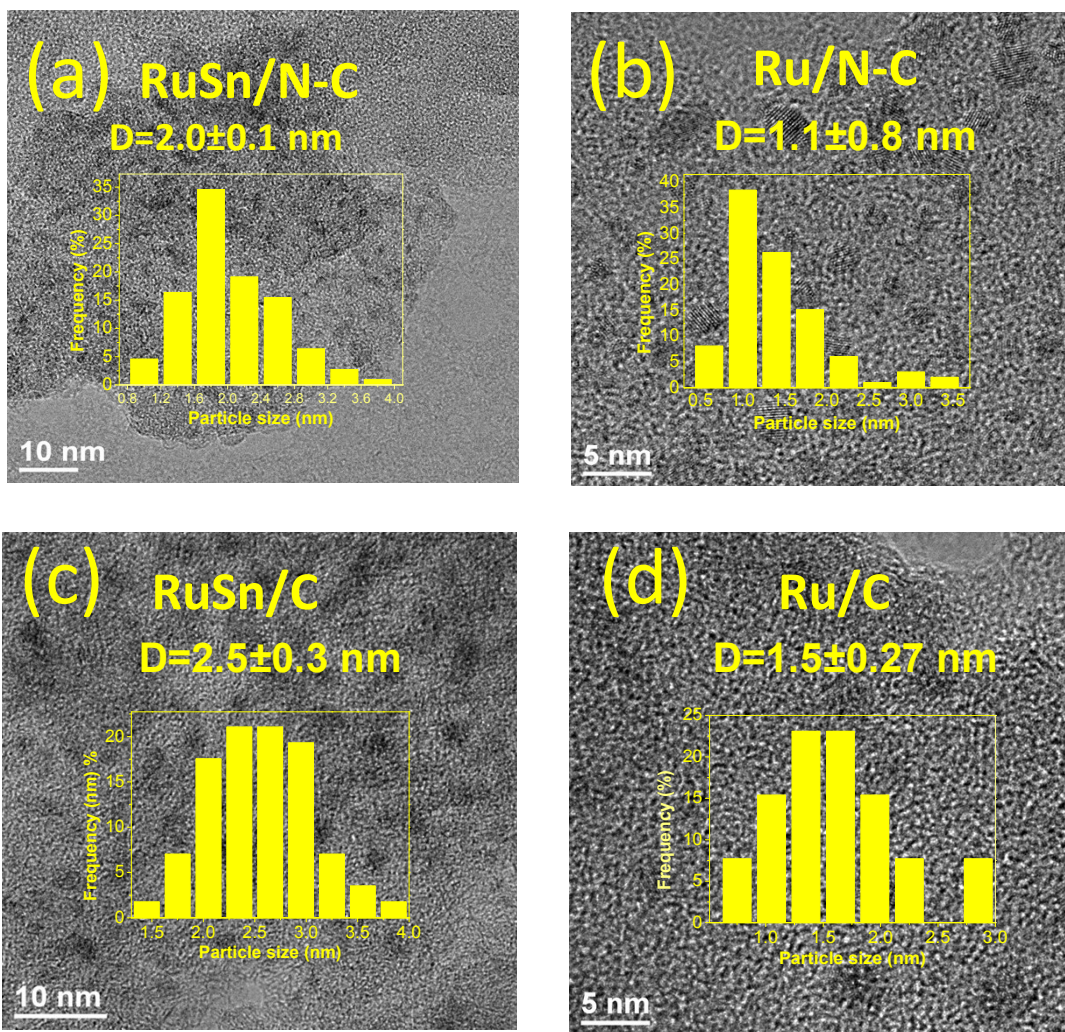


Fig. S5 TEM images of (a) RuSn/N-C, (b) Ru/N-C, (c) RuSn/C, and (d) Ru/C catalysts.

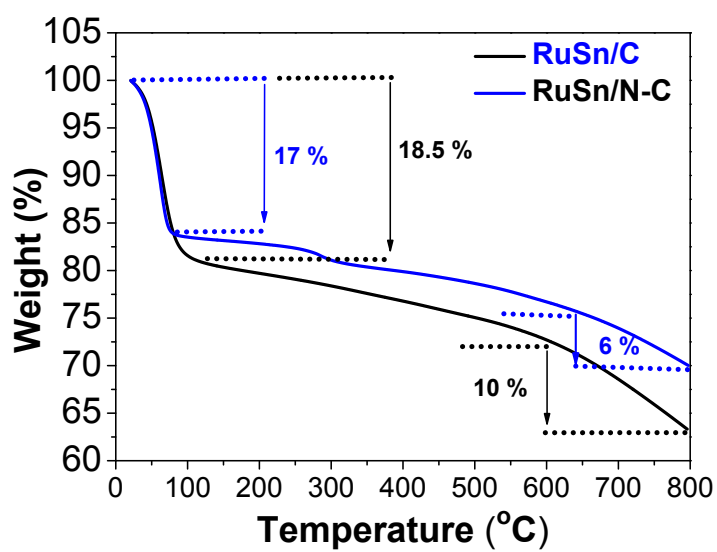


Fig. S6 The TGA profiles of RuSn/C and RuSn/N-C catalysts.

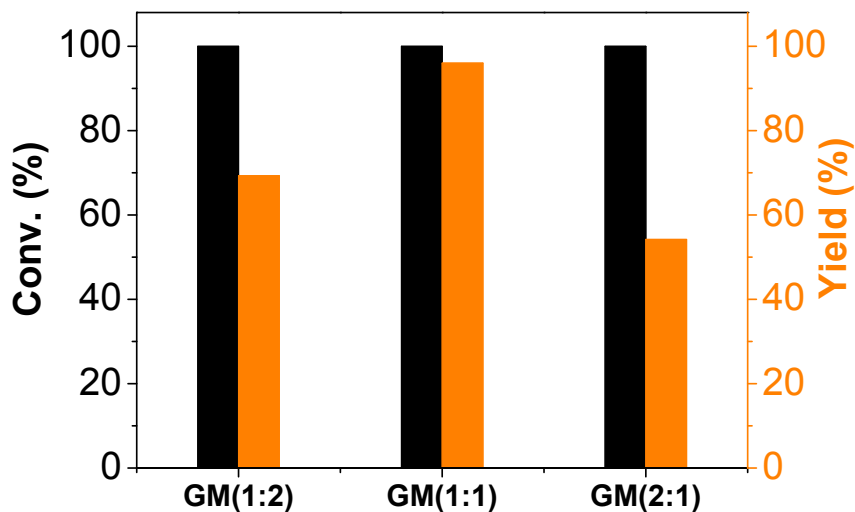


Fig. S7 The yield of stearyl alcohol from stearic acid conversion in the different ratio of glucose (G) and melamine (M). Reaction conditions: RuSn/N-C catalyst (each Ru and Sn 2.5 wt%, 0.1 g), stearic acid (0.4 g), 140 °C, water (80 mL), H₂ (5 MPa), 6 h, stirring at 500 rpm.

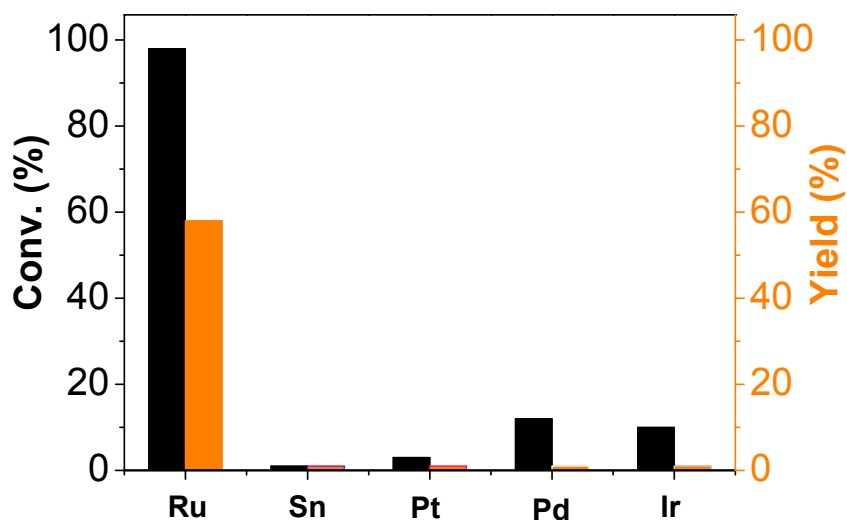


Fig. S8 The conversion of stearic acid and yield of stearyl alcohol in different metals (M). Reaction conditions: M/N-C catalyst (M 2.5 wt%, 0.1g), stearic acid (0.4 g), water (80 mL), 140 °C, H₂ (5 MPa), 6 h, stirring at 500 rpm.

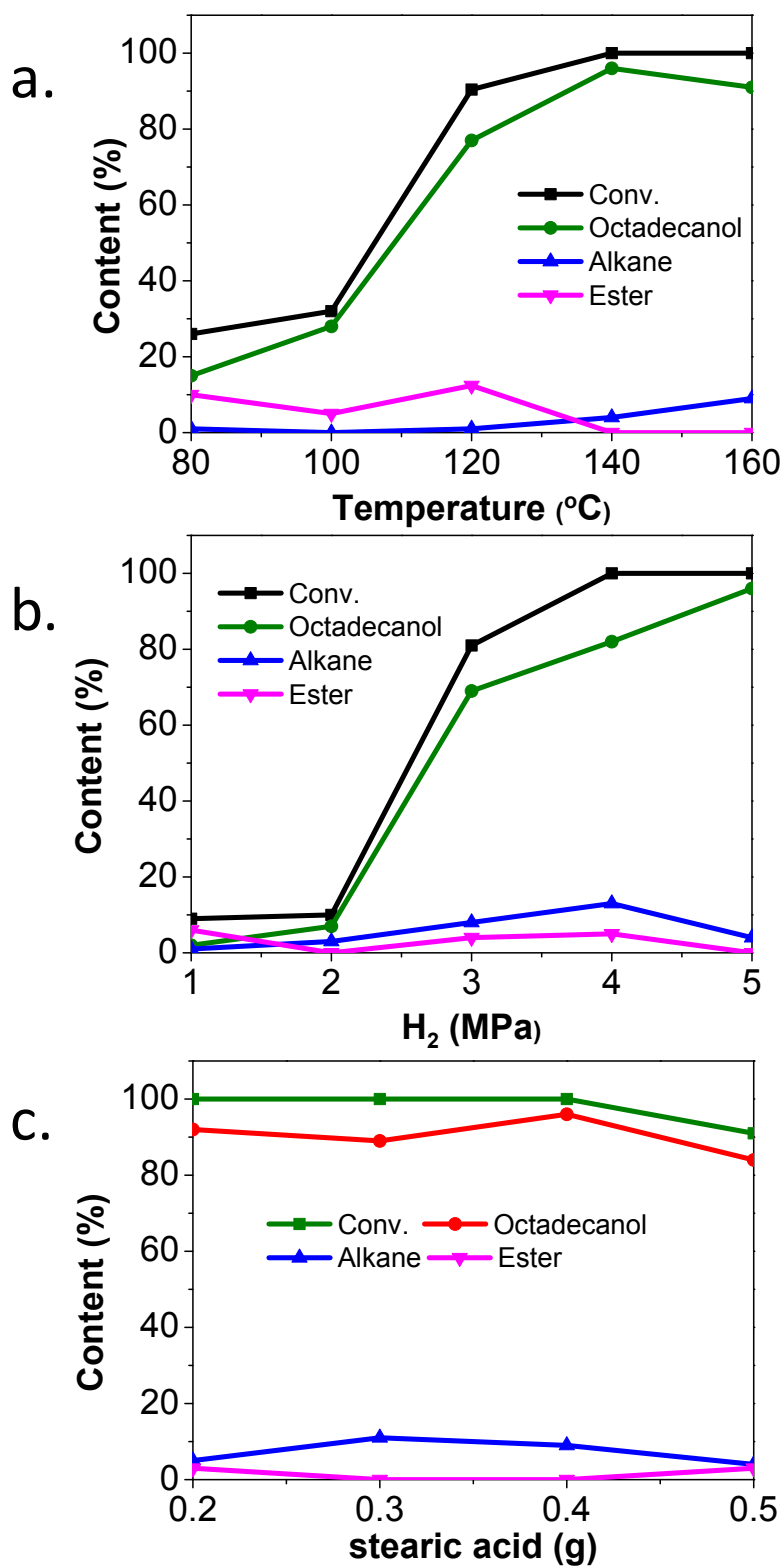


Fig. S9 Effect of (a) temperature at 5 MPa H₂, (b) H₂ pressure at 140 °C, and (c) substrate to catalyst ratio for the stearic acid conversion. General reaction conditions: RuSn/N-C catalyst (2.5 wt% Ru and 2.5 wt% Sn, 0.1g), stearic acid (0.4g), 140 °C, water (80 mL), 6 h, stirring at 500 rpm.

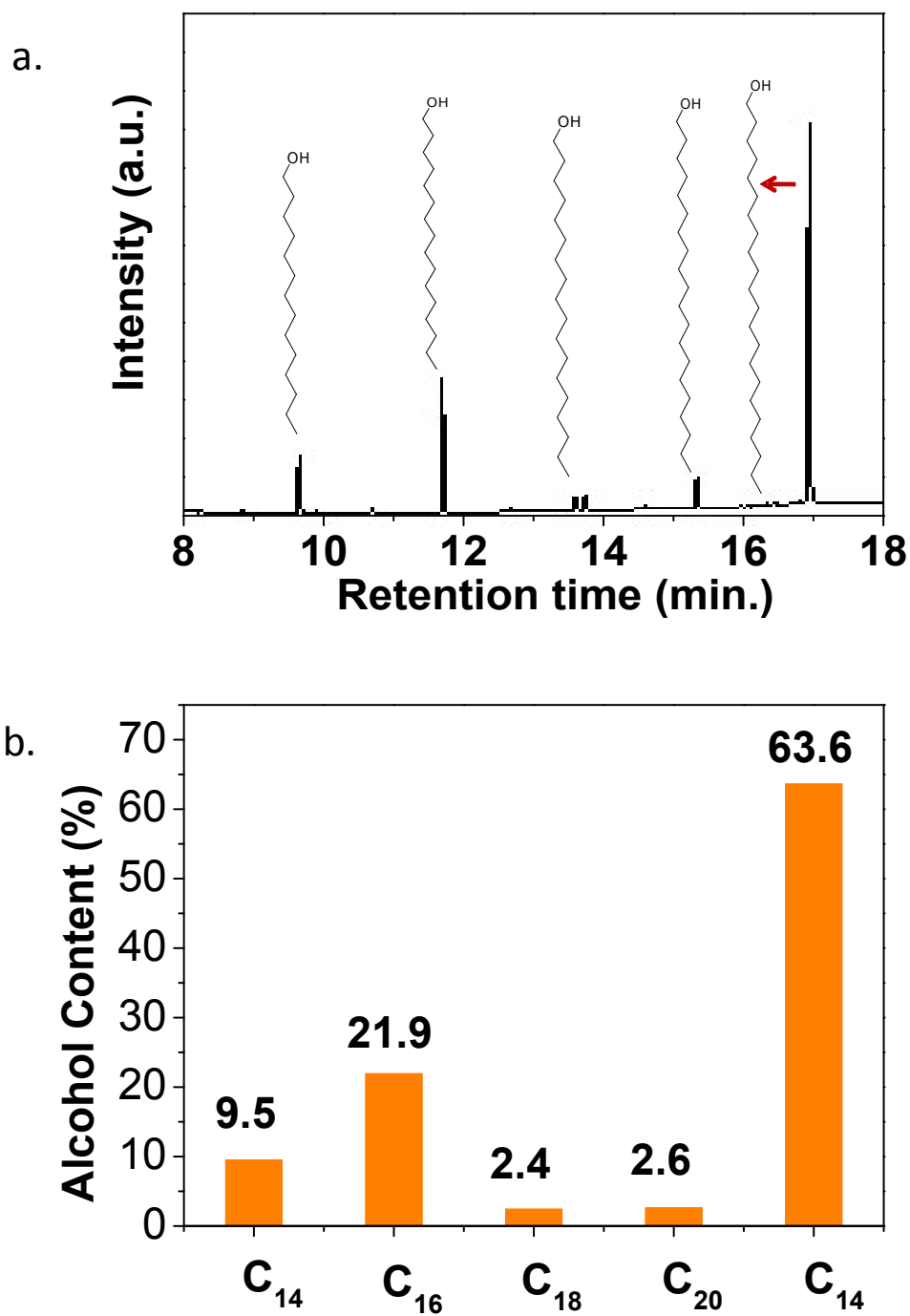


Fig. S10 (a) The product distributions of algae oil conversion and (b) the alcohol contents detected by GC coupled with MS. Reaction conditions: algae oil (0.4 g), RuSn/N-C (0.1 g), water (80 mL), 140 °C, 6 h, H₂ (5 MPa), stirring at 500 rpm.

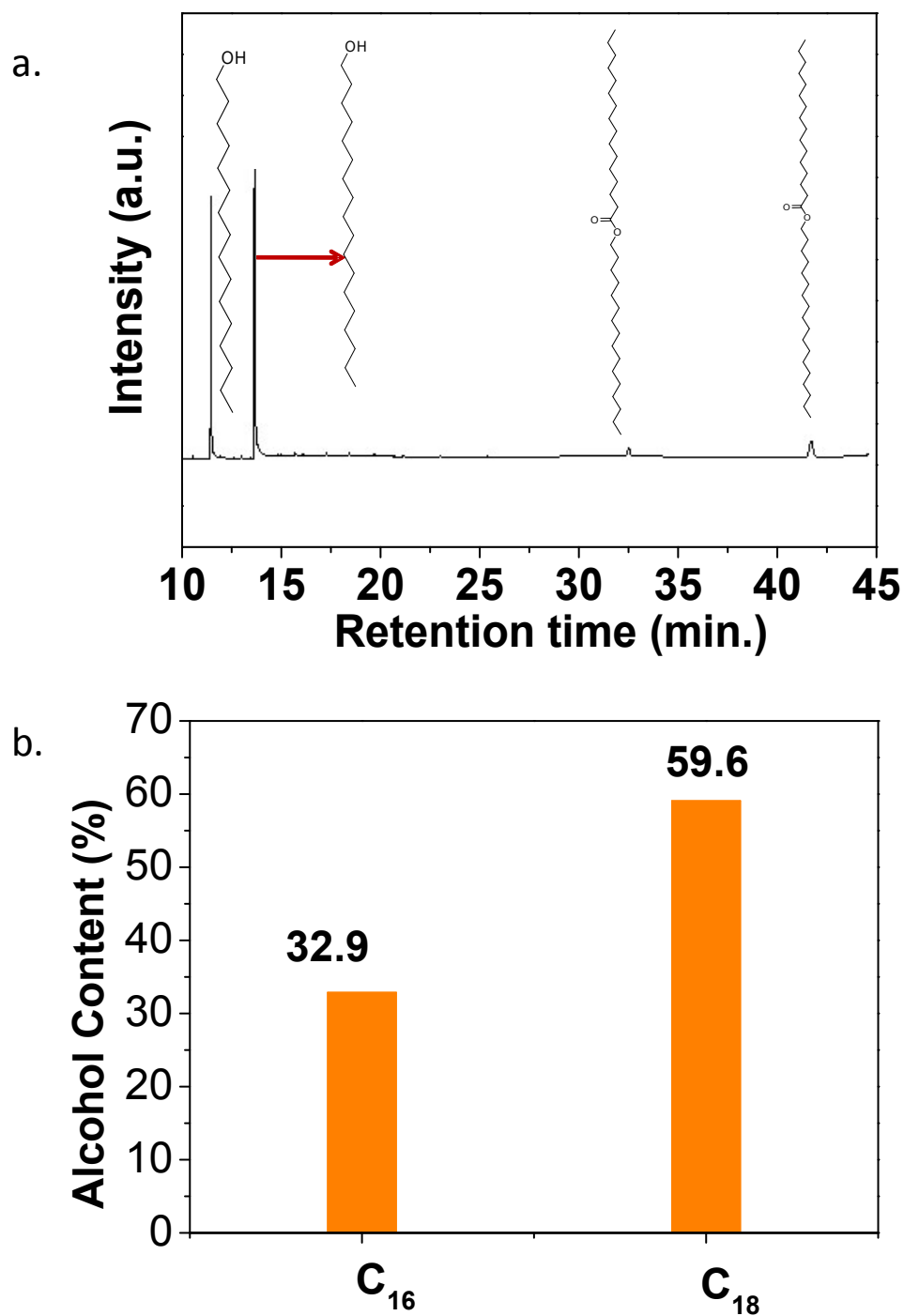


Fig. S11 (a) The product distributions of palm oil conversion and (b) the alcohol contents detected by GC coupled with MS. Reaction conditions: palm oil (0.4 g), RuSn/N-C (0.1 g), water (80 mL), 180 °C, 6 h, H₂ (5 MPa), stirring at 500 rpm.

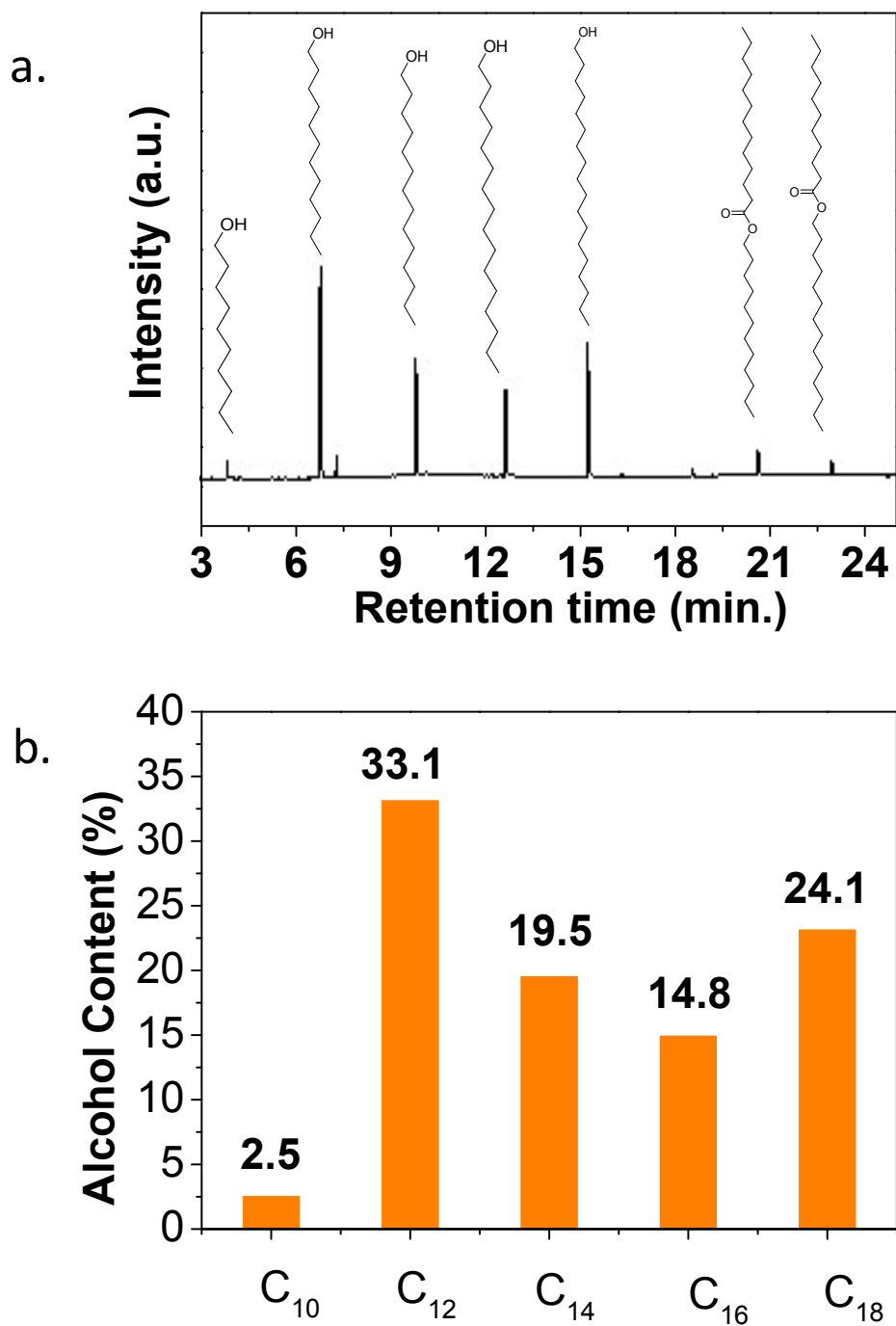


Fig. S12 (a) The product distributions of coconut oil conversion and (b) the alcohol contents detected by GC coupled with MS. Reaction conditions: coconut oil (0.4 g), RuSn/N-C (0.1 g), water (80 mL), 180 °C, 6 h, H₂ (5 MPa), stirring at 500 rpm.

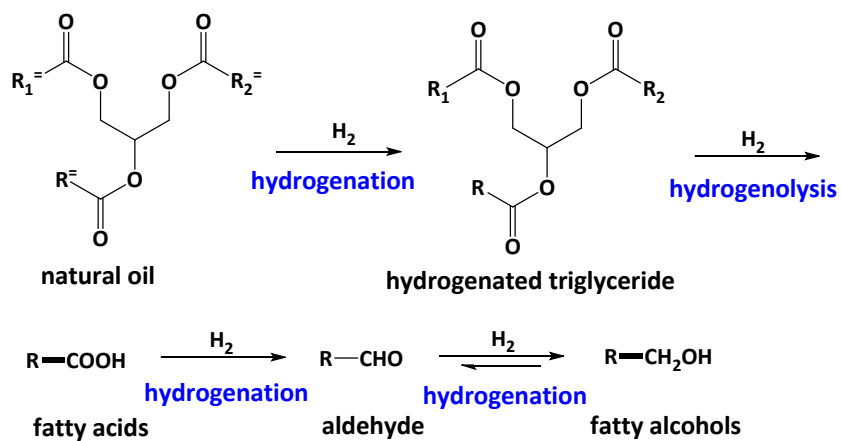


Fig. S13 Mechanism for the formation of fatty alcohol from natural oil.

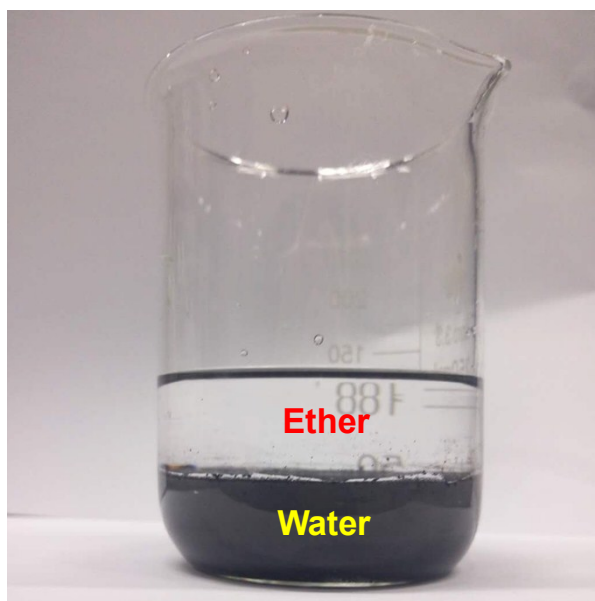


Fig. S14 The dispersion of RuSn/N-C catalyst was in the bottom hydrophilic water layer after the hydrogenation of fatty acid, and the upper layer was hydrophobic ether layer.



Fig. S15 Recycling test of hydrogenation of algae oil over RuSn/N-C catalyst (treated by sequential hydrogen reduction). Reaction conditions: algae oil (1.0 g), RuSn/N-C (0.3 g), water (80 mL), 140 °C, 6 h, H₂ (5 MPa), stirring at 500 rpm.

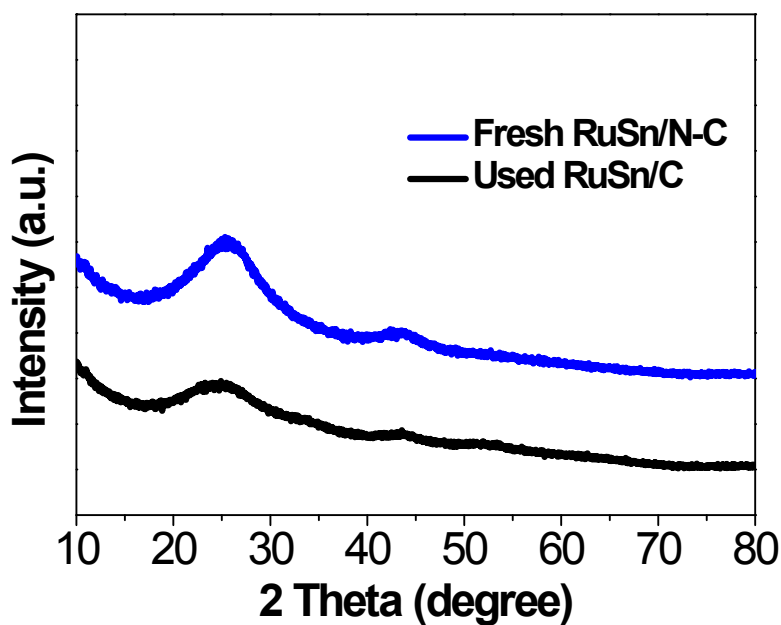


Fig. S16 XRD spectra of the fresh and used catalyst.

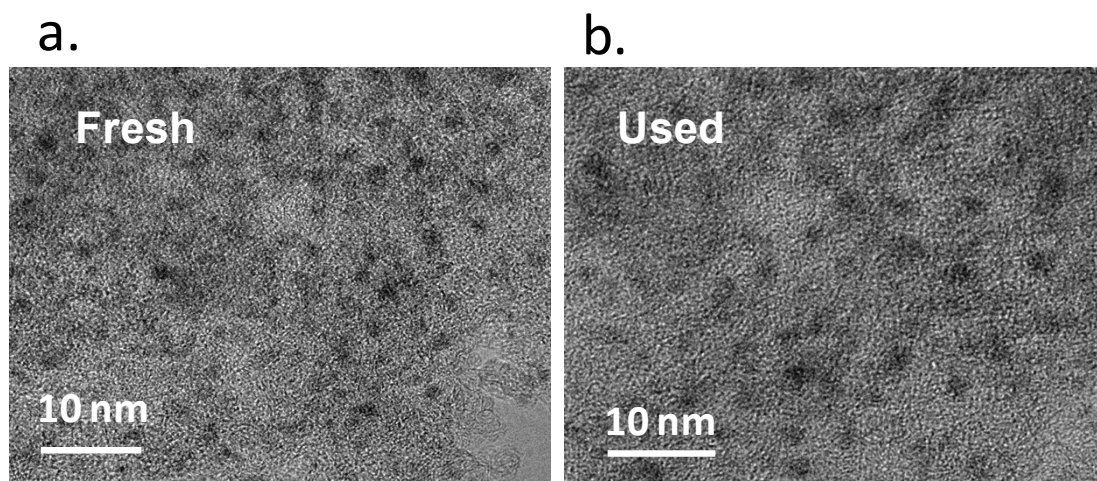


Fig. S17 The TEM images of (a) fresh and (b) used RuSn/N-C catalyst.

Table S1. Textural properties of the catalysts.

Entry	Catalysts	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
1	RuSn/N-C	474	0.2772
2	Ru/N-C	667	0.3767
3	RuSn/C	1165	0.7476
4	Ru/C	1227	0.7588

Table S2. The fatty acid composition (%) in algae oil.

C _{14:0} ⁿ	C _{16:0}	C _{16:2}	C _{17:0}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}	C _{22:2}	C _{22:5}	C _{22:6}
0.61	14.62	0.13	0.42	2.71	1.44	5.21	0.17	1.12	16.5	45.37

ⁿ The nomenclature represents the number of carbon atoms and the number of C=C double bonds: for instance the alkyl chain of the present fatty acid contains 14 carbon atoms and no double bond. Algae oil contains fatty acids 88.3 wt % and alkenes as 11.7 wt %.

Table S3. The fatty acid composition (%) in palm oil.

C _{16:0} ⁿ	C _{18:0}	C _{18:1}	C _{18:2}
41.57	8.26	40.74	9.43

Palm oil contains 41.57 wt % C16 saturated fatty acid, 8.25 wt % C18 saturated fatty acid and 9.43 wt % C18 unsaturated acid .

Table S4. Fatty acid composition (%) in coconut oil.

C _{8:0} ⁿ	C _{10:0}	C _{11:0}	C _{12:0}	C _{13:0}	C _{14:0}	C _{15:0}	C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}
7.18	5.77	0.017	49.21	0.023	18.56	0.0094	8.863	0.0136	2.60	6.385	1.369

Coconut oil contains 49.21 % C12, 18.56 wt % C14, 7.18 wt % C8, 5.77 wt % C10, 0.017 % C11, 0.023 % C13, 0.0094 wt % C15, 8.863 wt % C16, 2.6005 wt % C18 saturated fatty acids while 0.0131 wt % C16 and 7.754 wt % C18 unsaturated fatty acids.