Supplementary file

Glycerolysis of Palm Oil Using Copper Oxide Nanoparticles Combined With Homogeneous Base Catalyst

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Experimental section

NMR studies

^{13}C NMR. Spectra were recorded on high resolution spectrometers (AVANCE III; Bruker, Karlsruhe, Germany) operating at a carbon–13 frequency of 125 MHz. Spectra were recorded for concentrations of 10–20% (w/v) (50–100 mg of sample in 0.5 mL of chloroform–*d*) using 5 mm NMR tubes at controlled temperature of 30±0.1°C in the broadband proton decoupling mode. Full ^{13}C NMR spectra were obtained with the following acquisition parameters: 16 K data points, spectral width 200 ppm, acquisition time 0.37 s, relaxation delayed 5 s, pulse width 45° and 256–3000 scans. High resolution carbonyl spectra were recorded with 16 K data points, spectral width 10 ppm, acquisition time 12–20 s, relaxation delayed 5 s and pulse width 45–90°. Free induction decays (FIDs) were transformed by zero filling up to 32 K data points to yield a digital resolution of 0.05–0.08 Hz per point. All FIDs, prior to Fourier transformation (FT), were filtered using an exponential multiplication (0.2–0.4 Hz line broadening) for sensitivity enhancement. The peak intensities of the high resolution ^{13}C NMR carbonyl spectra were accurately quantified using the Linesim (Bruker) curve resolution program. The ^{13}C NMR was presented in Figure S1.

^{1}H NMR. Samples (20 μL) were placed in 5 mm NMR tubes and dissolved in chloroform–*d* (0.7 mL) and DMSO–d_6 (20 μL). The chemical shifts were referred

indirectly to TMS signal (δ=0.0 ppm) by assigning the residual signal from $CHCl_3$ to 7.26 ppm. One dimensional spectra were recorded on Bruker AM 400 instrument (Central Laboratory, Universiti Malaysia Pahang, Malaysia) operating at 500 MHz. The ^{1}H NMR was presented in Figure S2 and Table S1.

Qualitative characterization by NMR

^{13}C–NMR studies

^{13}C NMR spectroscopy is a useful method for the identification of MG and DG in the glycerolysis products. The experiment was carried out in the range of 0–175 ppm and three patterns were recorded as (a) before the glycerolysis reaction of palm oil, (b) after reaction with NaOH (1 h) and (c) after reaction with CuO–nano+NaOH catalysts (1 h) (Figure S1). However, analysis on shift and intensity of the signals from two different carbons in the ester groups at 60–75 ppm and 172–175 ppm is more informative as shown in the figure. It is evident from the figure that the signals of initial TG fragment were practically disappearing and simultaneously new peaks of MG and DG were appearing. In the ^{13}C NMR spectra of palm oil, the signals of carboxyl groups at 173.15 and 172.75 ppm and that at 62.1 and 68.89 ppm correspond to carbon atoms of the glycerol fragment (Figure S1). These signals were related to TG (Figure S1a) which also reported by other researchers [1-5]. In the spectrum of the products, the peaks at 63.35, 65.0 and 70.18 ppm and at 174.3 and 173.95 correspond to the carbon atoms with attached hydroxyl groups in MG and that at 173.5 ppm was related to DG (Figure S1b). All these signals can be assigned to HO–**C**H_2–CH(OH)–CH_2OOR (63.35 ppm), HO–CH_2–CH(OH)–**C**H_2OOR (65.00 ppm) and HO–CH_2–**C**H(OH)–CH_2OOR (70.18 ppm) [1, 3, 5]. A close observation points out that some less intense peaks of DG grew up as intermediates.

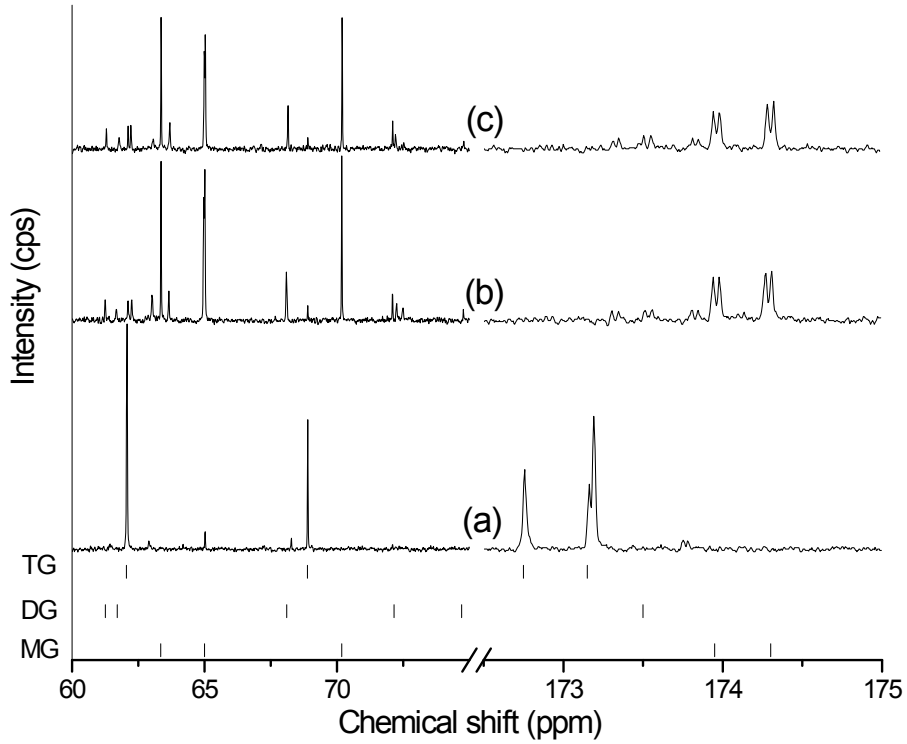

Figure S1. ^{13}C-NMR spectra of glycerolysis reaction of palm oil with chemical shifts of the products: (a) before reaction; (b) after reaction with NaOH catalysed and (c) after reaction with CuO-nano+NaOH catalysed. A break is shown in the figure from 75 to 172.5 ppm.

^{1}H–NMR studies

Figure S2 shows ^{1}H–NMR spectra of (a) before the glycerolysis reaction of palm oil, (b) after reaction with NaOH (1 h) and (c) after reaction with CuO–nano+NaOH catalysts (1 h), respectively. The proton resonances of TG, DG and MG were assigned according to literature data [3, 5-7] and presented in Table S1. It can be seen that, the ^{1}H–NMR spectra of the sample catalysed by NaOH and CuO–nano+NaOH are almost identical. In general, major changes were seen in the region of 3.5–4.5 ppm, where signal of TG (L) were disappearing and signals of MG (G, I and K) and DG (H, J and M) were appearing. Apart from that, it is important to note that TG has specific signals (L and P) due to the protons present in the glyceryl backbone. The ^{1}H–NMR spectra signals of protons of acyl group chain are similar for all samples. However, small differences in chemical shifts of protons supported on carbon atoms in alpha and beta positions in relation to the carbonyl group (signals C1, C2, E1 and E2) were occurred.

Therefore, signals (C1 and E1) and (C2 and E2) identified as acyl groups of TG and other glycerides (MG and DG), respectively. The obtained result is in consistent with ^{13}C–NMR outcomes (Figure S1).

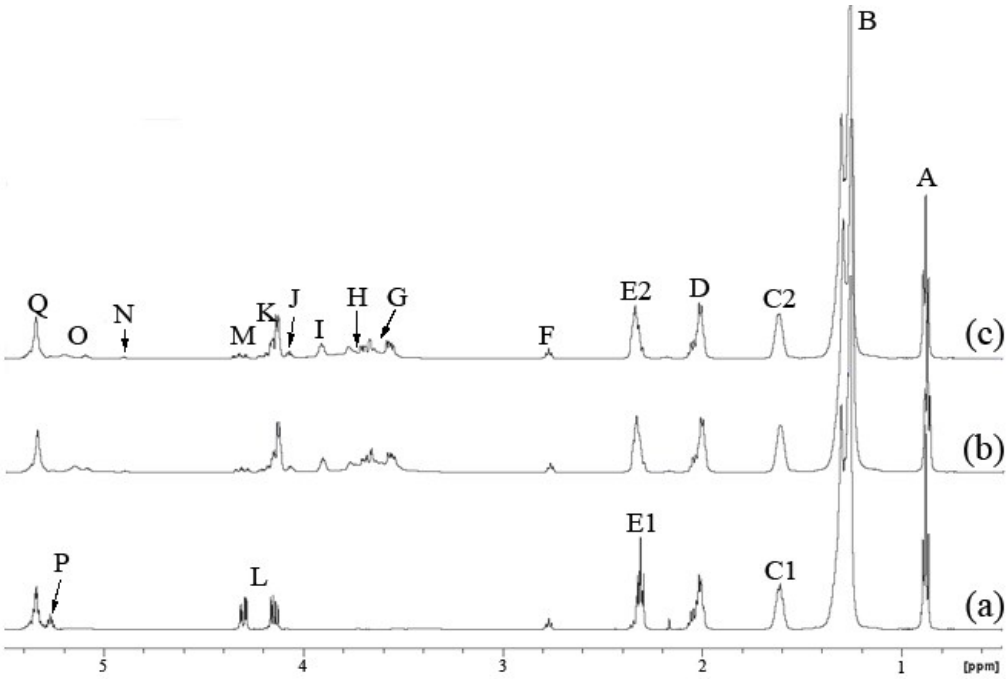

Figure S2. ^{1}H–NMR spectra of glycerolysis reaction of palm oil with chemical shifts of the products: (a) before reaction; (b) after reaction with NaOH and (c) after reaction with CuO-nano+NaOH.

Table S1. Chemical shifts and assignment of main resonances in ^{1}H–NMR spectra of palm oil and products of glycerolysis reaction (see Figure S2).

Signal	Chemical shifts (ppm)	Multiplicity	Type of proton	Compound
A	0.884	t	–C**H**$_3$	Saturated, monounsaturated acyl groups and FA
B	1.255	m	–(C**H**$_2$)n–	Acyl groups and FA
C1	1.610	m	–OCO–CH$_2$– C**H**$_2$–	Acyl groups in TG
C2	1.620	m	–OCO–CH$_2$– C**H**$_2$–	Acyl groups in 1,2–DG
D	1.90–2.18	m	–C**H**$_2$–CH=CH–	Acyl groups and FA
E1	2.28–2.37	dt	–OCO–C**H**$_2$–	Acyl groups in TG

E2	2.33–2.34	m	–OCO–C**H**$_2$–	Acyl groups in 1,2–DG, 1,3–DG, 1–MG and FA
F	2.77	t	=CH–C**H**$_2$–CH=	Di–unsaturated acyl groups and FA
G	3.645	ddd	ROCH$_2$–CHOH–C**H**$_2$OH	Glyceryl group in 1–MG
H	3.73	m	ROCH$_2$–CH(OR')–C**H**$_2$OH	Glyceryl group in 1,2–DG
I	3.91	m	ROCH$_2$–C**H**OH–CH$_2$OH	Glyceryl group in 1–MG
J	4.05–4.24	m	ROC**H**$_2$–C**H**OH–C**H**$_2$OR'	Glyceryl group in 1,3–DG
K	4.18	ddd	ROC**H**$_2$–CHOH–CH$_2$OH	Glyceryl group in 1–MG
L	4.22	dd,dd	ROC**H**$_2$–CH(OR')–C**H**$_2$OR''	Glyceryl group in TG
M	4.30	ddd	ROC**H**$_2$–CH(OR')–CH$_2$OH	Glyceryl group in 1,2–DG
N	4.90	m	HOCH$_2$–C**H**(OR)–CH$_2$OH	Glyceryl group in 2–MG
O	5.08	m	ROCH$_2$–C**H**(OR')–CH$_2$OH	Glyceryl group in 1,2–DG
P	5.27	m	ROCH$_2$–C**H**(OR')–CH$_2$OR''	Glyceryl group in TG
Q	5.28–5.46	m	–C**H**=C**H**–	Acyl groups and FA

Abbreviations: d: doublet; t: triplet; m: multiplet; TG: triglyceride; DG: diglyceride; MG: monoglyceride; FA: fatty acid.

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