Electronic supplementary information for:

Electro-hydrogenation of biomass-derived levulinic acid to γ -valerolactone via the magnetic heating of a Ru nanocatalyst

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1. Experimental details

1.1. Materials

Iron (III) sulphate hydrate ($Fe_2(SO_4)_3 \cdot xH_2O$, Sigma-Aldrich), iron (II) sulphate hydrate ($FeSO_4 \cdot 7H_2O$ 92%, Alfa-Aesar), ammonium hydroxide (NH_4OH 25% solution, J.T. Baker), citric acid monohydrate (ACS 99-102%, Alfa-Aesar), acetone (reagent grade, Carlo-Erba), glucose (D-glucose 99%, Alfa-Aesar), ruthenium (III) 2,4-pentadionate ($Ru(C_5H_7O_2)_3$ 97%, Sigma-Aldrich), 2-propanol (ACS reagent grade, VWR), Ru/C (5 wt% Ru, Sigma Aldrich) and levulinic acid ($C_5H_8O_3$ 98%, Alfa-Aesar) were used received.

1.2. Magnetic field applicator

An Ambrell (USA) HTG-6000 high frequency generator was used as an AC source. Copper-tube coil (Induktio d.o.o., Slovenia) of inner diameter of 40 mm, height of 52 mm and 6 turns resonates at 273 kHz when connected to the generator. Generator and coil were water cooled using closed compressor cooler OBE 003.

1.3. Catalyst synthesis

Citric-acid-coated iron oxide nanoparticles MN-CA were synthesised by hydrothermal treatment of precipitated Fe³⁺/Fe²⁺ ions at 120 °C followed by the adsorption of the citrate ion in an aqueous solution using a previously published method [S1, S2]. In brief, to the 100 ml of the Fe³⁺ (0.113 mol/L) and Fe²⁺ (0.135 mol/L) a 150 ml of ammonium hydroxide was added in a single rapid pour, during vigorous mixing using a magnetic stirrer. The precipitate was transferred to a Teflon-lined stainless-steel autoclave and heated for 2h at 120 °C. After cooling down naturally, the nanoparticles (MN) were washed 3 times using dilute ammonium hydroxide solution having pH value of 10 and a permanent

magnet to separate the nanoparticles. After last washing, the MN were diluted with DDI water to the final volume of 60 ml. To this slurry, 2.5 ml aqueous solution of citric acid (0.5 g/L) was added and then the pH value was set to 5.2 with a diluted solution of ammonium hydroxide. The suspension was heated under reflux and kept at 80 °C for 1.5 h while constantly stirred using a magnetic stirrer. After cooling down naturally, pH of the suspension was adjusted to the value of 10 using a diluted solution of ammonium hydroxide. The MN-CA nanoparticles were flocculated by addition of 200 ml of acetone, separated by a permanent magnet and liquid part discarded. The MN-CA nanoparticles were washed 2 times with acetone. The MN-CA were dispersed in 5 ml of DDI water, the suspension was heated to 80 °C for 30 min to remove residual acetone and centrifuged at 5000 rpm to remove agglomerates. The concentration of MN in the resulting colloidal aqueous suspension was 161 g/L. The MN-CA suspension was diluted with DDI water and glucose was added. The final concentration was 9 g/L of MNs and 90 g/L of glucose. A concentrated solution of NaOH was added to adjust the pH to a value of 10. A total of 800 mL of the suspension was transferred to a 1-litre stainless-steel Parr autoclave equipped with a stirrer. The suspension was treated at 180 °C for 12 h. The brown flock (MN-aC) was magnetically separated, washed several times with DDI water and dried at 80 °C in an an oven. The dried powder MN-aC was annealed in a tubular furnace at 500 °C for 6 h, followed by annealing at 600 °C for 2h in an atmosphere of Ar. The black powder (MN-C) was milled as a 2-propanol slurry in an agate planetary ball mill for 2h. The obtained suspension of MN-C was diluted with 2-propanol, and a concentrated, pink solution of Ru(III) 2,4-pentadioante was added to reach the final concentrations of 1 g/L of MN-C and $5\cdot 10^{-4}$ mol/L of Ru³⁺ in 2-propanol. A total of 800 mL of the suspension was transferred to the 1-litre stainless-steel Parr autoclave, bubbled with Ar for 30 min and heated to 150 °C for 10 min while vigorously stirring. The black, highly magnetic product (MN-C-Ru) was rapidly separated from the solution using a permanent magnet. The remaining solution was clear, colourless and with an acetone smell, indicating complete reduction of the Ru³⁺ to Ru⁰. The MN-C-Ru was washed 5 times with pure 2-propanol and dried in vacuum at room temperature. Based on the XRF analysis the MN-C-Ru contained 4.5±0.5 wt.% of Ru.

The same procedure was used to prepare catalyst with nominally 2 wt.% of Ru loading (MN-C-2Ru). For this the amount of added Ru(III) 2,4-pentadioante was suitably reduced. Based on the XRF analysis the MN-C-2Ru contained 1.6±0.2 wt.% of Ru.

1.4. Catalytic tests

0.45 g of the MNC-C-Ru was weighed into the round-bottom glass pressure vessel (Q-Tube-Purging - 35-SS, LabTech[™]), 1.5 g of levulinic acid and 1.5 g of isopropanol were added. The vessel was closed,

flushed first with Ar for 5 times and then with H_2 for 5 times. Finally, the vessel was pressurized with H_2 to 1 MPa. During the whole hydrotreatment the total pressure was maintained constant at the value of 1 MPa using the H_2 .

1.4.1. Conventional heating

The vessel was placed in an oil bath, heated to the desired temperature and kept for 2 hours during vigorous stirring (1480 rpm, *P*=650 W) using a magnetic stirrer. After 2 hours the vessel was left to cool naturally to room temperature. The amount of consumed electrical energy in Wh within 2 hours of heating was measured using the X4-Life 700379 Inspector III Energy Consumption Monitor. The catalyst was separated using a handheld permanent magnet and the clear liquid part was decanted. The liquid was analysed by GC-QMS (Ultra 2010, Shimadzu, Japan) after dilution with acetone (>99.9% Sigma-Aldrich).

For control purposes homogeneous reaction was performed at 80 °C and 120 °C using the same amount of levulinic acid and isopropanol and otherwise the same conditions except that no catalyst was added. To evaluate the effect of iron oxide nanoparticles MN on LA conversion the same reaction was performed at 120 °C using 0.45 g of MN.

1.4.2. AC-heating

The vessel was placed in the centre of the inductor coil (6 turns) with the vessel's bottom lifted from the surface of the magnetic stirrer by approx. 1 mm. The field of μ_0 H=46 mT was turned (640W) on during vigorous stirring (1480 rpm) using a magnetic stirrer. The surface temperature of the vessel was continuously recorded using fibre-optic probe. The temperature reached a steady state of 85 °C after 25 min. Liquid samples were periodically sampled at final temperature for the analysis. After selected time into the reaction passed the vessel was left to cool naturally to room temperature. Subsequently the gas phase was evacuated to pre-vacuumed gas burette while the lines and reactor vessel were further washed by pressurizing it (2 bar) with Ar (5.0 Messer), hence collecting all the process gas content in the gas burette. Collected gas was then analysed using micro-GC (Inficon Fusion) with Rt-Molsieve 5A (0.25mm, 10m, Ar carrier gas) module to determine H₂ and N₂ content and Rt-Q-Bond (0.25mm, 8m, He carrier gas) modules to determine CO₂ content. The catalyst was separated using a handheld permanent magnet and the clear liquid part was decanted. The liquid was analysed by GC-QMS (Ultra 2010, Shimadzu, Japan) after dilution with acetone (>99.9% Sigma-Aldrich). The catalyst was washed five times with pure isopropanol and recycled four times using the same conditions and loadings. Hydrodeoxygenations of furfural and hydroxymethyl furfural were conducted under identical conditions as hydrotreatments of levulinic acid, using MN-C-2Ru nanocatalyst.

Stirring the reaction mixture is necessary to achieve the transfer of hydrogen into the liquid phase and to contact the reactants with the catalyst. In our case a magnetic stirrer was used to achieve the mixing. Magnetic and conductive materials heat in AC fields and therefore the magnetic stirrer and hot plate (turned off, used to rotate the stirrer) could also supply heat to the reaction mixture. We conducted an independent experiment to determine to what extent the magnetic stirrer and hotplate contribute to the heating under identical conditions as used for the hydrotreatment. The glass pressure vessel was loaded with 2-porpanol and a magnetic stirrer (without MN-C-Ru catalyst). The vessel was placed at exactly the same positon within the coil as during the hydrotreatment (approx. 1 mm above the surface of the hotplate). The vessel was left open and the fibre optical sensor was used to monitor the temperature of the isopropanol continuously. The stirrer was set to 1480 rpm and the field of μ_0H =46 mT was turned on. After 30 min the temperature increased by just 5 °C. The experiment proves that the increase of the temperature during the hydrotreatment described above is solely due to heating of MNP-C-Ru under the influence of an AC field.

1.3. Catalyst characterization

X-ray powder diffraction patterns (XRD) were collected using a PANalytical X'Pert PRO MPD diffractometer with a monochromator in the direct beam. DIFFRACplus Topas^{*} software was used to estimate average crystallite size by a fundamental parameters approach to line-profile fitting. A scanning transmission electron microscope (STEM) Cs-corrected Jeol ARM 200CF STEM operated at 80 kV was used to observe the MN@C-Ru catalyst, deposited on a copper-grid-supported lacy carbon foil. During the analysis HAADF and BF detectors were used simultaneously at 68-180 and 10-16 mrad collection semi angles, respectively. To minimize the specimen drift, images were taken several hours after the insertion of the sample in the microscope and at least 20 minutes after the last sample positioning to minimize the goniometer drift. The chemical composition was analyzed using a Jeol Centurio EDXS system with 100 mm² SDD detector and Gatan GIF Quantum ER Dual EELS system. A transmission electron microscope (TEM) Jeol JEM 2100 operated at 200 kV was used to observe MN-CA, MN-C and MN-C-Ru and to estimate size of the iron oxide and Ru nanoparticles. Empirical, number-weighted, particle-size-distribution functions were estimated from the TEM images. The particle size *d* is given as an equivalent diameter—the diameter of a circle having the same area as the imaged particle. The average particle size *d*_{TEM} and its standard deviation was obtained from Gaussian

fit of an empirical number-weighted distribution function. Nitrogen adsorption/desorption isotherms were measured for the sample MN-C-Ru at liquid-nitrogen temperature using a Nova 2000e (Quantachrome) nitrogen-sorption analyser. Prior to the measurement the sample was degassed over night at 120 °C in a vacuum. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation with nitrogen-adsorption data in the P/P_0 range between 0.05 and 0.3. Room-temperature magnetization curves of the sample MN-C-Ru as dry powder were measured with a vibrating-sample magnetometer (VSM) LakeShore 7307 VSM. The Ru content in the MN-C-Ru was non-destructively determined by using an energy-dispersive X-ray fluorescence spectrometer (EDXRF) comprised of a Ge semiconductor detector (GLP-16195/10-P, ORTEC, Oak Ridge, U.S.A) with an energy resolution of 401 eV at 60 keV, a spectroscopy amplifier (M2020, Canberra, Meriden, U.S.A.), ADC (M8075, Canberra, Meriden, U.S.A.) and a PC-based MCA (S-100, Canberra, Meriden, U.S.A.). For the excitation annular Am-241 radioactive source (25 mCi, Isotope Products Laboratories. U.S.A) was used. Quantification was performed utilizing the in-house-developed QAES (Quantitative Analysis of Environmental Samples) software [S3, S4]. For the analysis, sample powders were diluted with cellulose and pressed into a pellet of 24 mm in diameter. Ru surface concentration was determined by CO pulsed adsorption using an AutoChem II Chemisorption Analyser (Micrometrics). The sample was first reduced at 473 K for 2 h in stream of 10% H₂ in Ar. Afterwards it was cooled to 273 K in stream of He and pulsed oxidised with O₂. After oxidation, the sample was again reduced and cooled to 273 K in stream of He. At 273 K CO pulses were gradually increased until saturation. The total amount of adsorbed CO was obtained by integration of the peak (saturation). Using the CO: Ru = 1:1 stoichiometry the Ru surface concertation in the nanocatalyst was determined to be 23.5 μ mol/g.



Figure S1. TEM image of the citric-acid-coated cubic-spinel iron-oxide magnetic nanoparticles (MN-CA). Insets are Selected area electron diffraction (SAED) and the empirical size distribution of nanoparticles (circles) with a Gaussian fit (curve).

In SAED pattern only reflections characteristic for cubic spinel iron oxide (Space group) Fd-3m are present (due to clarity only indices of sharpest refractions are shown). Among iron oxides, only so called magnetite and maghemite crystalize in cubic spinel structure. Structure of magnetite Fe_3O_4 can be represented by the $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$ formula, where the round and square brackets represent tetrahedral and ochtahedral lattice sites, respectively. If all the iron in the cubic spinel is in the 3+ state, the cation vacancies compensate for the oxidation of Fe^{2+} and the structure of maghemite γ -Fe₂O₃ can be represented by the $(Fe^{3+})[Fe^{3+}_{1.67}\square_{0.33}]O_4$ formula, where \square represents vacancies. Our previous study [S1] showed that the nanoparticles synthesized under identical conditions as the MN-CA contained only 0.09 of the Fe^{2+} per formula unit, while 1 would correspond to magnetite. Therefore, we assume the magnetic nanoparticles composing the MN-CA, MN-aC, MN-C and MN-C-Ru are consistent with maghemite structure.



Figure S2. TEM images of the precursor particles MN-aC at lower (a) and higher (b) magnification. Inset in (a) is Selected area electron diffraction (SAED) pattern acquired from the central region shown in figure (a) and enlarged in figure (b). In SAED pattern only reflections characteristic for cubic spinel iron oxide (Space group Fd-3m) are present. The SAED is dim because of relatively high thickens of the carbonaceous matrix.



Figure S3. TEM images of the support MN-C at lower (a) and higher (b) magnification. Insets in (a) are SAED pattern and the empirical size distribution of nanoparticles (circles) with a Gaussian fit (curve). In SAED pattern only reflections characteristic for cubic spinel iron oxide (Space group Fd-3m) are present.



Figure S4. XRD powder patterns of the MN-C (black) and MN-C-Ru and after being used in 5 consecutive magnetically heated hydrotreatments of LA (black). Both patterns are indexed according to the cubic spinel structure (Space Group Fd3m).



Figure S5. TEM image of the MN-C-Ru.



Figure S6. Empirical distribution function (dots) fitted with Gaussian (line) of equivalent diameters d_{TEM} of Ru nanoparticles in the MN-C-Ru.



Figure S7. Nitrogen adsorption isotherm for the fresh MN-C-Ru (red) and after being used in 5 consecutive magnetically heated hydrotreatments of LA (black).

The isotherm in Figure S7 is a typical Type I isotherm [S5]. BET method can be applied to estimate the specific surface area S_a , but caution is needed in the presence of micropores (i.e., with Type I isotherms and combinations of Types I and II or Types I and IV isotherms). It may be impossible to separate the processes of monolayer from multilayer adsorption and micropore filling. With microporous adsorbents, the linear range of the BET plot may be very difficult to locate. The so called Rouquerol method [S6] was used to estimate the so called apparent specific surface area, S_a =309 m²/g (C constant was approx. 70).

Figure S8. Room-temperature magnetisation curves of fresh MN-C-Ru (black) and after being used in 5 consecutive magnetically heated hydrotreatments of LA (red).

Figure S9. Image of the pressure reactor setup within the inductor coil during operation. The white dashed line shows the liquid's level before magnetic heating and red circle shows the position of the fibre-optic sensor attached to the surface of the pressure vessel (fibre-optic sensor not visible on the image).

Ferrimagnetic materials exhibit hysteretic magnetization behaviour due to energy barrier (combined effect of magneto-crystalline, shape and surface anisotropy) separating minimal energy magnetization state. Domain structure further contributes of hysteretic behaviour. However, in our case magnetic nanoparticles are well separated and in such size range that they can be considered as single-domain particles. Curve such as in Figure S8 is called static hysteresis as H field during the course of measurement changes on a much longer time scale as magnetisation dynamics and each field point represents equilibrium magnetization. In general, the area of such hysteresis curve equals energy lost as heat in one closed cycle (H field from $+H_{max}$ to $-H_{max}$ and back to $+H_{max}$). When AC field is used its amplitude is usually much smaller as the field needed to saturate the sample. For example, from Figure S8 it appears that approx. 500 mT is needed to saturate our MN-C-Ru while for magnetic heating 46

mT AC field was used. Therefore, the sample can not reach saturation and in addition the H field changes so fast (frequency of 271 kHz) that magnetization can not follow it and lags to a certain degree. This results in a significant change in the shape of the so-called dynamic hysteresis curve. The specific shape and consequently the area enclosed depends on the AC-field amplitude and its frequency. The area and heat released in one cycle is therefore significantly smaller that static hysteresis implies. However, despite the modest amount of heat released in once cycle the number of cycles is high, in our case 273 000 cycles per s which results in significant amount of heat generated by the sample.

2. Kinetic modelling details

The kinetic model developed and reported in our previous works [S7-S9] was used to a) determine relevant kinetic parameters for conventionally heated (oil bath) experiments, b) to use these parameters for predicting the catalyst surface temperature during the magnetic heating, based on the experimentally-determined activity.

The model took into consideration surface reaction rate (r_i^{surf}) of each reaction *I*, depending on the surface reaction rate constant (k^{surf}) and coverage of corresponding reactant *j* (Θ_j) and hydrogen (for hydrogenation reactions) adsorbed to active sites, defined in Eq.1.

$$r^{surf}_{\ i} = k^{surf}_{\ i} \Theta_j \Theta_H \tag{1}$$

Adsorption rate (r_j^{ads}) and desorption rates (r_j^{des}) of each compound *j* were adopted from our previous works, and were again proved not to be rate limiting, as expected. Adsorption rate depends on the adsorption rate constant (k^{ads}) , its concentration in liquid phase (C_j^L) , and concentration of vacant sites (Θ_{VS}) , defined in Eq.2. Similarly, desorption rate depends on desorption rate constant (k^{des}) , and coverage of *j* adsorbed to active sites (Θ_j) , defined in Eq.3.

$$r^{ads}_{\ j} = k^{ads}_{\ j} C^L_j \Theta_{VS} \tag{2}$$

$$r_{j}^{des} = k_{j}^{des} \Theta_{j} \tag{3}$$

The influence of surface temperature on rate constants for surface reactions was described by modified Arrhenius equation as presented in Eq. 4;

$$k_{i}^{surf}(T) = A_{i}^{surf} exp_{i}^{[i]}\left(\frac{Ea_{i}}{RT}\right)$$
(4)

80 °C was selected as a reference temperature, as it was the set temperature of the first conventionally-heated experiment. The reaction rate constants were calculated at every time increment to also take into account the non-isothermal segment of the process (heat-up ramp).

Based on the reaction pathway network (Figure 3b), the molar balances for gaseous hydrogen (C_{H2}^{G}) concentration in the headspace volume of the reactor V_{G} (Eq. 5), components in liquid phase (Eq. 6a, Eq. 6b for hydrogen) and surface sites (Eq. 7) are formulated as follows:

$$\frac{dC_{H2}^{G}}{dt} = -k_{GL}a \left(\frac{p_{H2}}{H} - C_{H2}^{L}\right) \frac{V_{L}}{V_{G}}$$
(5)

$$\frac{dC_j^L}{dt} = -r_j^{ads} + r_j^{des} \frac{n_{TS}}{V_L}$$
(6a)

$$\frac{dC_{H2}^{\ L}}{dt} = + k_{GL} a \left(\frac{p_{H2}}{H} - C_{H2}^{\ L} \right) - r_{\ j}^{ads} + r_{\ j}^{des} \frac{n_{TS}}{V_L}$$
(6b)

$$\frac{d\Theta_j}{dt} = r_j^{ads} \frac{V_L}{n_{TS}} + r_j^{des} + \sum_i^I \pm r_i^{surf}$$
⁽⁷⁾

By solving the set of ordinary differential equation with Runge-Kutta solver in Matlab software, concentration profiles were calculated and optimal kinetic parameters were obtained and collected in Table T1 after the regression analysis was complete (Nelder–Mead method for coarse regression and Levenberg–Marquardt method for fine tuning of the parameters and to calculate Jacobian matrix and 95% confidence intervals.). Further details and used parameters related mass transfer, hydrodynamic and thermodynamics can be found in our previous works [S7-S9].

Figure S10. Experimental and modelling results for LA hydrotreatment with conventional heating at a) 80 °C and b) 120 °C. Conditions: 0.45 g of MNC-C-Ru, 1.5 g of LA, 1.5 g of i-PROH, 1 MPa H₂, 1480 rpm.

Table	T1.	Calculated	kinetic	parameters	and	TOF	for	LA	hydrotreatment	over	MN-C-Ru	under
conve	ntio	nal heating a	at 80 °C i	and 120 °C (T	he hi	ghest	t valı	Jes	of TOFs are repor	ted).		

		Pre-exponential	Activation	Turnover	Turnover	
i	r .	factors	Energies (Ea.)	Frequencies	Frequencies	
	/ i	$(A_{\rm i}),$	$k \operatorname{Imol}^{-1}$	(TOF_i) at 80 °C,	(TOF_i) at 120 °C,	
		min ⁻¹	KJ IIIOI	min ⁻¹	min ⁻¹	
1	$k^{surf}_{1}\Theta_{LA}$	90±4	31.7±0.9	60	188	
2	$k^{surf}_{2}\Theta_{LA}\Theta_{H2}$	13900±200	21.8±0.5	71	150	
3	$k^{surf}_{3}\Theta_{iPL}\Theta_{H2}$	13200±300	93.0±0.8	21	195	
4	$k^{surf}_{4}\Theta_{HPA}$	$>> k_2$	n.a.	$\approx TOF_2$	\approx TOF ₂	
5	$k^{surf}_{5}\Theta_{HPL}$	>>k ₃	n.a.	≈TOF ₃	\approx TOF ₃	

Figure S11. Concentration profile for a homogeneous reaction hydrogenation of levulinic acid in isopropanol. LA: levulinic acid, iPL: isopropyl levulinate. Reaction conditions: LA (1.5 g, 13 mmol), 2-propanol (10.5 g), $H_2 1$ MPa. Lines serve as a guide to the eye.

Figure S12. Concentration profile for a conventionally heated (120 °C) hydrogenation of levulinic acid in isopropanol of MN. LA: levulinic acid, iPL: isopropyl levulinate. Reaction conditions: 0.45 g MN, LA (1.5 g, 13 mmol), 2-propanol (10.5 g), H_2 1 MPa. Lines serve as a guide to the eye.

Figure S13. Concentration profile for a magnetically heated hydrogenation of levulinic acid in isopropanol over MN-C support. LA: levulinic acid, iPL: isopropyl levulinate. Reaction conditions: 0.45 g MN-C, LA (1.5 g, 13 mmol), 2-propanol (10.5 g), H_2 1 MPa. Lines serve as a guide to the eye.

Figure S14. TEM image of the MN-C-2Ru.

Figure S15. Concentration profiles for a magnetically heated hydrogenation of levulinic acid in isopropanol over MN-C-2Ru. LA: levulinic acid, iPL: isopropyl levulinate. Reaction conditions: LA (1.5 g,

13 mmol), 2-propanol (10.5 g), H_2 1 MPa. (a) 0.225 g MN-C-2Ru, (b) 0.450 g MN-C-2Ru and (c) 0.900 g MN-C-2Ru. Lines serve as a guide to the eye.

Figure S16. Concentration profiles for a magnetically heated hydrotreatment of hydroxymethyl furfural in n-butanol over the MN-C-2Ru. HMF: hydroxymethylfurfural, BHMF: 2,5-bishydroxymethalfuran, 2-HM-5-MF: (5-methyl-2-furyl)methanol, DMF: dimethylfuran and Others: chemical identity of compounds could not be unambiguously determined by GC-MS however the GC-MS suggests that this fraction is composed of di-, tri- and oligomers of HMF. Reaction conditions: HMF (1.5 g, 12 mmol), 1butanol (10.5 g), H₂ 1 MPa. Lines serve as a guide to the eye.

Figure S17. Concentration profiles for a magnetically heated hydrotreatment of furfural in n-butanol over the MN-C-2Ru. FU: furfural and FA: furfuryl alcohol. Reaction conditions: FU (1.5 g, 15 mmol), 1-butanol (10.5 g), H_2 1 MPa. Lines serve as a guide to the eye.

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