Electronic Supplementary Information (ESI) for

Catalytic valorization of the acetate fraction of biomass to aromatics and its integration into the carboxylate platform

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Experimental details

Chemicals and materials

All reagents and materials were used as received. $Cu(NO_3)_2 \cdot 3H_2O$ (99.999% Cu) and silicon carbide (100 mesh) were obtained from Strem. $ZrO(NO_3)_2 \cdot xH_2O$ (99%), urea (99-100.5%), concentrated nitric acid (65%), butanoic acid (99%), mesitylene (98%) and heptane (99%) were obtained from Sigma-Aldrich. Acetone (99.99%) was obtained from Fisher Chemical. Glacial acetic acid (100%) and concentrated sulfuric acid (95-97%) were obtained from Merck. ZrO_2 was obtained from AlfaAesar. Water was purified using a Millipore Milli-Q Advantage A10 water purification system to a resistivity higher than 18 MΩ·cm. Quartz wool was obtained from Ohio Valley Specialty Company. Synthetic air (99.999%), hydrogen (99.999%), helium (99.9999%), argon (99.9999%), nitrogen (99.999%), 10% hydrogen (99.999%) in argon, 2% N_2O (99.998%) in helium, 10% CO_2 (99.998%) in helium and methane (99.9995%) were obtained from Carbagas.

For the production of acetic and butanoic acid, *Lactobacillus pentosus* (DSM-20314) and *Clostridium tyrobutyricum* (DSM-2637) were purchased from DSMZ, Germany. *Trichoderma reesei* Rut-C30 (D-86271) was purchased from VTT, Finland. MRS broth was obtained from BD Difco, Switzerland. Reinforced clostridial medium was obtained from VWR, Switzerland. Phosphoric acid, sodium hydroxide, hydrochloric acid, urea, peptone, yeast extract, KH_2PO_4, $(NH_4)_2SO_4$, $FeSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ were obtained from Sigma-Aldrich. Beech wood (*Fagus sylvatica)* was harvested in winter 2015/16 from a forest in Messen, SO, Switzerland (donated by the Forstbetrieb Bucheggberg) and chipped in April 2016 to the size of G30 wood chips (max edge length: 85mm, max cross section: $3cm^2$).

Catalyst preparation

Zirconia (ZrO_2) was prepared by a modified method from Tsoncheva et al.[1] The ZrO_2 support was prepared by precipitation of $ZrO(NO_3)_2 \cdot xH_2O$ with urea. In a typical preparation, 5 L of water was acidified with 10 mL of concentrated nitric acid. 60 g of $ZrO(NO_3)_2 \cdot xH_2O$ was added and the solution was heated up to 90 °C while stirring. After the temperature stabilized, 160 g of urea were added and the solution was stirred for 15 h. The resulting precipitate was filtered and washed with water until there were no changes in the pH of the water before and after washing. The wet precipitate was dried in an oven at 110 °C overnight and subsequently calcined under flowing synthetic air at 450 °C (reached using a 2 °C/min ramp) for 3 h. The powder was stored in a nitrogen-filled glovebox prior to impregnation.

Cu supported on zirconia (Cu/ZrO_2) was prepared via incipient wetness impregnation. The desired amount of zirconia was taken out of the glovebox in a round-bottom flask fitted with a rubber septum. The appropriate amount of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in a solution of 0.1M nitric acid to facilitate solubilization. The solution was added drop-wise to the zirconia support up to the incipient wetness point. The wet catalyst was dried in an oven at 110 °C overnight.

Catalyst characterization

The loading and dispersion of the Cu/ZrO_2 catalyst was verified respectively via H_2 temperature-programmed reduction (TPR) and N_2O pulse titration in a Micromeritics Autochem II 2920 connected to an MKS Cirrus 2 Quadrupole mass spectrometer (MS). For each analysis, the cell was loaded with ~0.2 g of fresh catalyst. The carrier gas was helium flowing at 50 mL/min. H_2 TPR was performed by flowing 10% H_2 in Ar (50 mL/min) while a temperature ramp of 10 °C/min was applied until reaching 450 °C. Subsequently, N_2O (2% in He) was sent in pulses over the catalyst at 90 °C until no consumption was observed as determined by monitoring the mass 44 signal on the MS. A calcination under synthetic air (50 mL/min) was performed at 500 °C (reached using a 5 °C/min ramp) for 1 h, after which a second set of H_2 TPR and N_2O pulse titration experiments was carried out.

Subsequently, the total acid and basic sites of the Cu/ZrO_2 catalyst were verified respectively via NH_3 and CO_2 temperature-programmed desorption (TPD). The carrier gas was helium flowing at 50 mL/min. An initial H_2 TPR was performed by flowing 10% H_2 in Ar (50 mL/min) while a temperature ramp of 10 °C/min was applied until reaching 450 °C.

For NH_3 TPD, a flow of 1% NH_3 in He (50 mL/min) was maintained over the catalyst for 0.5 h at 50 °C, followed by a flow of He (50 mL/min) for 1 h to remove physisorbed NH_3. The TPD was then carried out by heating the sample to 450 °C (reached using a 10 °C/min ramp). Throughout the experiment, the MS was set to track mass 16.

For CO_2 TPD, a flow of 10% CO_2 in He (50 mL/min) was maintained over the catalyst for 0.5 h at 50 °C, followed by a flow of He (50 mL/min) for 1 h to remove physisorbed CO_2. The TPD was then carried out by heating the sample to 450 °C (reached using a 10 °C/min ramp). Throughout the experiment, the MS was set to track mass 44.

Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size and volume were measured using a Micromeritics 3Flex at liquid nitrogen temperature between 10^{-5} and 0.99 relative N_2 pressure. For each analysis, the cell was loaded with ~0.2 g of catalyst. The samples were dried at 120 °C (reached using a 2 °C/min ramp) under vacuum ($<10^{-3}$ mbar) for 4 h prior to analysis.

Catalytic testing

Upgrading of carboxylic acids was carried out in a fixed bed tubular reactor (OD=1/4 inch) in an up-flow configuration. Typically, 2g of catalyst was diluted with silicon carbide in a 1:1 ratio by volume using a graduated cylinder, and loaded into the heated zone of the reactor supported in place by silicon carbide beds and quartz wool plugs at both ends. The height of the catalyst bed was 10cm and started from the middle of the heated zone to enable the complete vaporization of the feed before it contacts the catalyst. The catalyst was reduced *in situ* under

H_2 flow (100 mL/min) at 450 °C (reached using a 2.5 °C/min ramp) for 4 h, then cooled to the desired reaction temperature. The aqueous feeds were prepared by diluting the desired carboxylic acid in water to the appropriate concentration. An SSI LS-class HPLC pump was used to deliver the feed. The pressure in the reactor was set using a Tescom back-pressure regulator, while the H_2 flowrate was controlled with a Brooks mass flow controller.

For regeneration of the catalyst, the feed flow was stopped and the catalyst was dried under Ar flow (100 mL/min) for 3 h at 400 °C and 10 bar and then cooled down. The catalyst was calcined under synthetic air (100 mL/min) at 500 °C (reached using a 2 °C/min ramp) for 5 h. An *in situ* reduction was performed prior to the run as described above.

Liquid samples were collected using a gas-liquid separator. Liquid phase analyses were carried out on an Agilent Technologies 7890A gas chromatograph equipped with a flame ionization detector (FID) and a HP-5 column. Online gas phase analyses were carried out on Agilent Technologies 7890A gas chromatograph with a gas sampling valve and a HP-PLOT Q column. Compound identifications were carried out on an Agilent Technologies 7890A gas chromatograph equipped with an Agilent Technologies 5977A MSD and a HP-5 UI column.

Prior to analysis, organic phase samples were diluted 10 times in heptane and aqueous phase samples were diluted 10 times in water. Using the ECN method[2], the response factor of a reference external standard measured using a calibration curve was used to calculate a modified response factor for each identified compound to quantify both liquid and gas phase products. We used the following ECN equation for our calculations:

$$RF_{comp} = RF_{ref} * \frac{ECN_{ref}}{ECN_{comp}}$$

where,

RF_{comp}: the modified response factor for the desired compound [mol/kg]

RF_{ref}: the measured response factor for the reference external standard [mol/kg]

ECN_{ref}: the effective carbon number of the reference external standard

ECN_{comp}: the effective carbon number of the desired compound

Organic phase products were quantified using mesitylene as the reference external standard. Aqueous phase products were quantified using acetone as the reference external standard. Gas phase products were quantified using methane as the reference external standard and assuming the ideal gas molar volume at 25 °C and 1 atm. The effective carbon numbers of all measured compounds are given in Table S1. All mass balances were closed above 90%, by estimating the mass of CO_2 formed from the 100% ketonization of the starting carboxylic acids. Carbon mole balances were closed above 80%, based on identified compounds from the chromatograms.

Conversion of acetone was defined as the ratio of the difference in the amount of acetone present in the product stream over the amount of acetone produced from acetic acid, assuming full conversion of acetic acid to acetone. The molar carbon distribution was defined as the moles of carbon of compounds with a particular carbon number divided by the total moles of carbon in the product stream. For molar carbon distributions involving the organic oil, only the carbon present in the organic oil was taken into consideration. In molar carbon distributions, "oxygenates" consisted of oxygenated molecules (molecules with at least 1 oxygen atom) in organic, aqueous and gas phases, unless specified to be only within the organic oil. "Hydrocarbons" consisted of molecules containing only carbon and hydrogen atoms.

The weight hourly space velocity (WHSV) was defined as the total mass flow rate of the feed divided by the mass of the catalyst in the reactor. The mass yield of the organic oil is defined as the mass of organic oil collected divided by the mass of carboxylic acids in the feed (not including water). The liquid hydrocarbon yield was defined as the moles of carbon present as liquid hydrocarbon divided by the moles of carbon of acetone produced from acetic acid,

assuming full conversion of acetic acid to acetone. The liquid hydrocarbon proportion within the organic oil was defined as the moles of carbon present as liquid hydrocarbons divided by the total moles of carbon in the organic oil.

For experiments with pure ZrO_2 (Fig. S1), the ZrO_2 used was purchased commercially from AlfaAesar.

Estimation of lower heating values (LHV) for the organic oil

The lower heating values (LHV) for the organic oil was first estimated by calculating the higher heating values (HHV) using the mass percentages of C, H and O for all identified compounds within the oil. The molecular formula and number of moles for each identified compound were used to calculate the mass of C, H and O for each compound as well as the total mass of identified compounds. The equation for estimating the HHV for liquid fuels was based on the correlation developed by Channiwala and Parikh.[3] The equation is as follows:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$$

Where,

HHV: the higher heating value [MJ/kg]

C: carbon mass percentage [wt%]

H: hydrogen mass percentage [wt%]

S: sulfur mass percentage [wt%]

O: oxygen mass percentage [wt%]

N: nitrogen mass percentage [wt%]

A: ash content [wt%]

Subsequently, the LHV was calculated from the HHV based on the calculation by ASTM.[4] The equation is as follows:

$$LHV = HHV - 0.2122H$$

Where,

H: hydrogen mass percentage [wt%]

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis

ICP-MS analyses were carried out by the EPFL Central Environmental Laboratory with an Agilent 8900 Triple Quadrupole ICP-MS. Around 300 mg of the organic oil was added into a Teflon tube, along with 8 mL of 65% nitric acid and 1 mL of 30% hydrochloric acid. The sample was subsequently digested in a microwave oven. The resulting liquid was filtered (0.45 μm) and diluted to 50 mL with water. The sample was again diluted by half with water prior to analysis.

Aviation fuel testing

The organic oil was sent to Intertek (Schweiz) AG for completion of the following tests. The oil was tested without any purification/work up as a 10 vol% blend with Jet A-1 fuel using standard methods specified by the Aviation Fuel Quality Requirements for Jointly Operated Systems (AFQRJOS): Issue 29 – Oct 2016. The following tests were performed:

- ASTM D1319: Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- ASTM D5453: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence

- ASTM D86: Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
- ASTM D4052: Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- ASTM D3338: Standard Test Method for Estimation of Net Heat of Combustion of Aviation Fuels

Electron microscopy imaging

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on a FEI Talos with 200 keV acceleration voltage. The fresh catalyst was dry impregnated on a Lacey carbon grid while the spent catalyst was deposited on a silicon nitride grid. Elemental mapping was performed in scanning transmission electron microscopy (STEM) mode using an energy-dispersive X-ray spectroscopy (EDX) detector.

Production of acetic and butanoic acid from beech wood

Steam pretreatment of beech wood. Beech wood chips (*Fagus sylvatica)* were air-dried and milled to a particle size of < 1.5 mm. The pretreatment was performed using a custom-built steam gun (Industrieanlagen Planungsgesellschaft m.b.H., Austria).[5] Saturated steam was added to pressurize and heat the biomass to 180 °C for 25 min. The hemicellulose was hydrolyzed to yield xylose and xylooligosaccharides in the prehydrolyzate. Acetyl-side chains bound to the xylopyranose backbone of the hardwood were released into the condensate. The condensate containing the hemicellulosic sugars and the acetic acid was extracted from the reactor under pressure, prior to slowly releasing the pressure and emptying the steam-gun. The recovered biomass was pretreated again at 230 °C for 14.1 min followed by an explosive pressure release to increase the enzymatic hydrolyzability of glucan. Following this procedure, the acetic acid concentration was 10 g/L.

Fungal and bacterial strains and culturing methods. *L. pentosus* precultures were grown at 30 °C in a MRS broth which contained (in g/L): peptone from casein, 10; meat extract, 10; yeast extract, 5; glucose, 20; Tween 80, 1; K_2HPO_4, 2; sodium acetate, 5; ammonium citrate, 2 and $MgSO_4 \cdot 7\ H_2O$, 0.2. The pH was adjusted to 6.2-6.5 with hydrochloric acid. *C. tyrobutyricum* precultures were grown at 37 °C in a reinforced clostridial medium composed of (in g/L): yeast extract, 13; peptone, 10; glucose, 5; soluble starch, 1; sodium chloride, 5; sodium acetate, 3; L-cysteine-HCl, 0.5; agar, 0.5. *T. reesei* precultures were grown at 28 °C in a Mandel medium which contained (in g/L): KH_2PO_4, 2; $(NH4)_2SO_4$, 1.4; $MgSO_4 \cdot 7\ H_2O$, 0.3; $CaCl_2 \cdot 6H_2O$, 0.4; urea, 0.3; peptone, 0.75; yeast extract, 0.25; and 1 mL/L trace element stock. The sterile filtered trace element stock contained (in g/L): $FeSO_4 \cdot 7\ H_2O$, 5; $MnSO_4 \cdot H_2O$, 1.6; $ZnSO_4 \cdot 7\ H_2O$, 1.4; $CoCl_2 \cdot 6H_2O$, 3.7 and 10 mL/L concentrated hydrochloric acid. To avoid precipitation, 100x $CaCl_2$ and $MgSO_4$ solutions were autoclaved separately before they were combined with the remaining ingredients.

Biofilm membrane reactor. Labfors (Infors HT, Switzerland) stirred-tank reactors with a working volume of 2.7 L were modified with a polydimethylsiloxane tubular, dense membrane (Mono-Lumen Tubing 1.58 x 3.18 x 0.80 (Dow Corning, USA)) (Fig. S12). The membrane was flushed with air at a rate of 368 mL/min. The temperature was maintained at 30 °C. Mandel medium with a solid loading of 3.86 wt% pretreated beech wood solids was used. The corresponding prehydrolyzate was linearly fed in 200 h. The pH was adjusted to 6.0 using 4 N phosphoric acid and 4 M sodium hydroxide. The subsequent secondary fermentation of the obtained lactate/acetate broth was performed in serum bottles under anaerobic conditions. The serum bottles were inoculated from a two-day liquid preculture of *C. tyrobutyricum* (5 vol%). The pH was adjusted to 6.0 by the addition of 4 N phosphoric acid. The final butanoic acid concentration was 9.5 g/L.

Purification of biomass-derived acetic and butanoic acid in water

The concentration of the aqueous acetic and butanoic acid broths were verified by high performance liquid chromatography (HPLC) using an Agilent 1260 Infinity HPLC equipped with a refractive index and UV detector.

Purification of acetic acid. The acetic acid solution from pretreatment was distilled to separate the acetic acid and water from any residual fermentation organic matter. The mixture was then neutralized with excess sodium carbonate. Subsequently, water was removed under vacuum using a rotary evaporator. The resulting salts were acidified with excess sulfuric acid. The mixture was then distilled at 125 °C to recover the acetic acid. A second purification of the acetic acid mixture was carried out with the same protocol. This purification method resulted in acetic acid with a purity of 40 wt% in water with a final recovery yield of 83 wt%.

Purification of butanoic acid. The fermentation broth contained butanoic acid partly in solution and partly in salt form. The butanoic acid in solution was purified with the same method as acetic acid. The residual solids from the initial distillation contained some butanoate salts. Excess water and sulfuric acid were added to the solids to convert the salts to butanoic acid. The solution was then distilled at 180 °C to recover the butanoic acid. This purification method resulted in butanoic acid with a purity of 40.3 wt% in water for a final recovery yield of 82 wt%.

References

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2 J. T. Scanlon and D. E. Willis, *J. Chromatogr. Sci.*, 1985, **23**, 333–340.
3 S. A. Channiwala and P. P. Parikh, *Fuel*, 2002, **81**, 1051–1063.
4 *ASTM D4809-18: Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)*, ASTM International, West Conshohocken, PA, 2018.
5 T. Pielhop, J. Amgarten, P. R. von Rohr and M. H. Studer, *Biotechnol. Biofuels*, 2016, **9**, 152.

Supplementary figures and tables

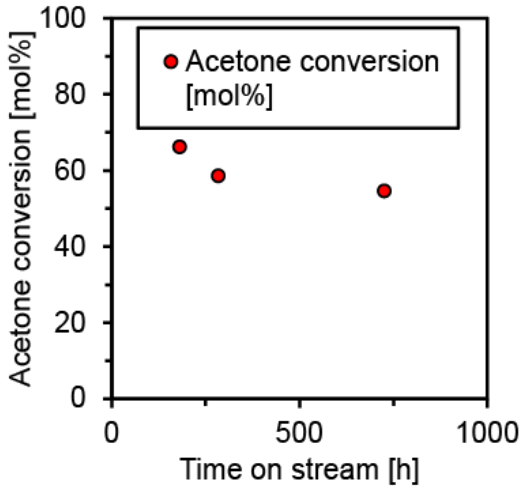

Fig. S1 Conversion of acetone as a function of time on stream during the upgrading of pure acetic acid over 2g commercial ZrO_2. (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1}, H_2 flow = 20 mL/min)

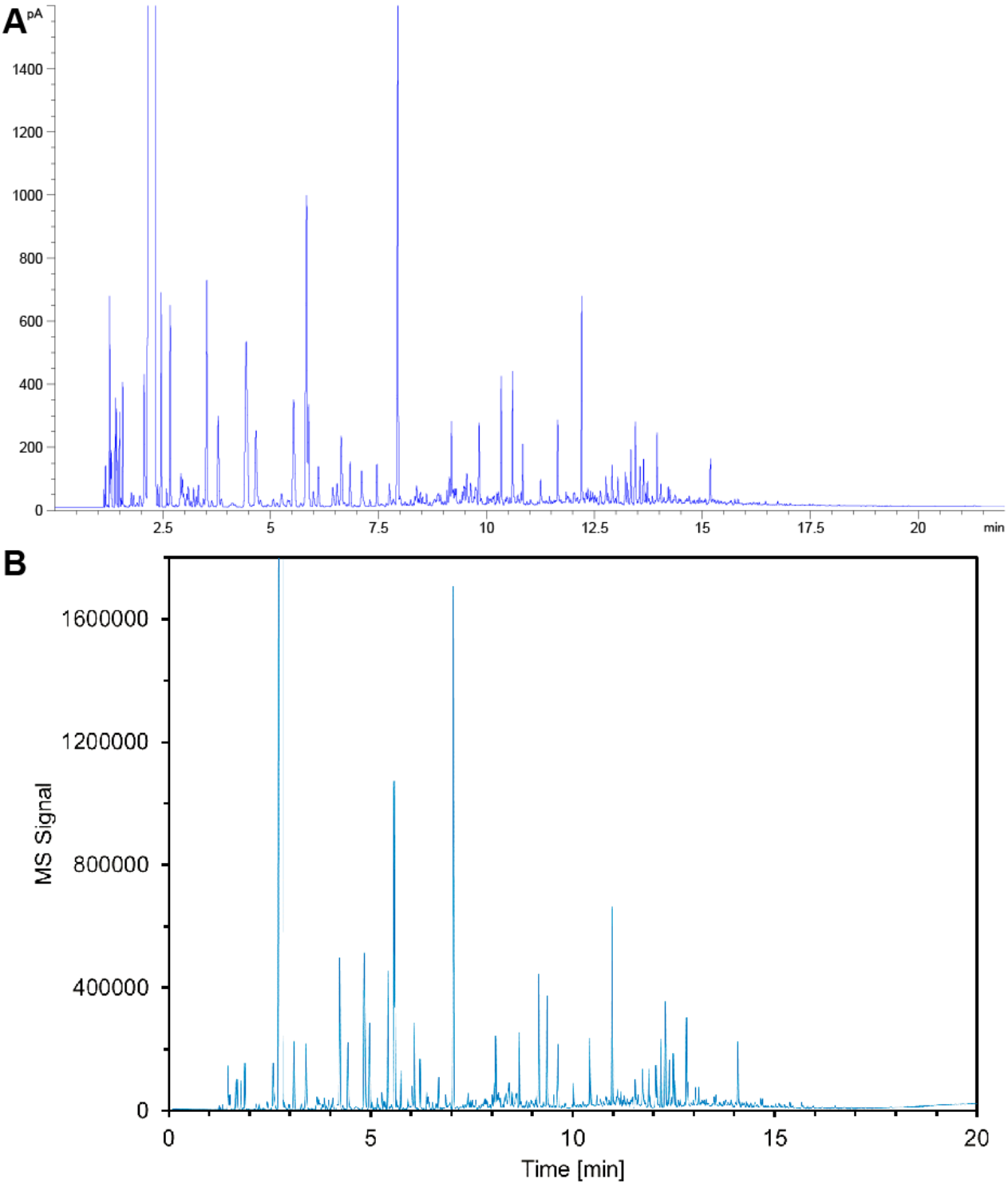

Fig. S2 A) GC chromatogram and B) GC-MS chromatogram of the organic oil during the upgrading of pure acetic acid (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1}, H_2 flow = 20 mL/min time on stream = 21.3 h, corresponding to Fig. 3D). Selected mass spectra for major product peaks and their references are shown in Fig. S3.

Table S1 List of identified compounds from the gas chromatogram (Fig. S2) of the organic oil during the upgrading of pure acetic acid (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1}, H_2 flow = 20 mL/min time on stream = 21.3 h, corresponding to Fig. 3D). Identification of compounds was performed by GC-MS, followed by peak matching with both chromatograms of GC and GC-MS, which uses the same column.

Compound name	Retention time [min]	Area	ECN
Propene	1.135	29.5858	2.9
Isobutylene	1.169	110.944	3.9
1-butene, 3-methyl	1.222	7.1959	4.9
Acetone	1.265	481.76	2
2-pentene	1.291	110.842	4.9
2-pentene	1.305	151.006	4.9
1-pentene, 4-methyl	1.394	260.223	5.9
2-butene, 2,3-dimethyl	1.431	344.384	5.9
1-pentene, 2-methyl	1.494	258.71	5.9
2-butanone	1.531	32.5655	3
2-pentene, 4-methyl	1.567	392.129	4.9
1,3-pentadiene, 2-methyl	1.72	4.9874	5.8
1,3-pentadiene, 2-methyl	1.743	7.5053	5.8
1-pentene, 2,4-dimethyl	1.768	66.7508	6.9
2-pentene, 3,4-dimethyl	1.818	63.2588	6.9
Hexane, 2-methyl	1.869	4.6911	7
Hexane, 2-methyl	1.898	32.0685	7
Hexane, 3-methyl	1.966	100.87	7
2-pentanone	2.064	763.818	4
1,3-pentadiene, 2,4-dimethyl	2.369	1.1792	6.8
2-heptene	2.395	57.1681	6.9
ethyl cyclopentane	2.597	62.1754	7
1-butanol, 3-methyl	2.624	12.9618	4.4
MIBK	2.678	820.255	5
3-hexene, 2,5-dimethyl	2.81	10.3455	7.9
1-heptene, 6-methyl	2.928	197.506	7.9
2-pentanol, 4-methyl	2.96	122.893	5.25
2-methyl, 2-heptene	2.993	67.1094	7.9
2-methyl heptane	3.064	58.6998	8
Toluene	3.097	108.376	7
cyclohexene, 1-methyl	3.154	27.3365	6.9
2-heptene, 6-methyl	3.219	93.848	7.9
cyclohexane, 1,3-dimethyl	3.284	48.5985	8
2-heptene, 6-methyl	3.332	124.96	7.9
cyclohexene, 4,4-dimethyl	3.449	43.2184	7.9
Cyclohexene, 3,5-dimethyl	3.525	1257.99	7.9

3-heptene, 4-methyl	3.643	40.5617	7.9
cyclopentene, 1,2,3-trimethyl	3.713	4.7957	7.9
Cyclohexene, 3,5-dimethyl	3.791	555.18	7.9
Cyclohexane, 1,3-dimethyl	3.862	57.7369	8
trans-2-methyl, 3-octene	4.127	22.0201	8.9
Cyclohexene, 3,5-dimethyl	4.439	1841.39	7.9
Cyclohexene, 3,5,5-trimethyl	4.665	643.293	8.9
Cyclohexane, 1,1,3-trimethyl	4.769	48.9398	9
2-pentanone, 3-ethyl	4.935	17.4872	6
1,3-cyclopentadiene, 5,5dimethyl-1-ethyl	5.067	56.7648	8.8
2,3-dimethyl-3-heptene	5.152	29.7884	8.9
1,1-dimethyl-4-methylenecyclohexane	5.257	128.87	8.9
1,3-cyclopentadiene, 5,5dimethyl-1-ethyl	5.402	37.6723	8.8
2,3-dimethyl cyclohexa-1,3-diene	5.436	33.539	7.8
Cyclohexene, 3,5,5-trimethyl	5.536	937.218	8.9
2-methyl 2-octene	5.704	20.236	8.9
m-xylene	5.826	2142.33	8
Cyclohexene, 3,3,5-trimethyl	5.874	560.924	8.9
4-heptanone	5.985	93.9678	6
Cyclohexene, 3,3,5-trimethyl	6.102	233.871	8.9
2-heptanone	6.434	129.95	6
1,3-cyclopentadiene, 5,5dimethyl-1-ethyl	6.536	139.836	8.8
Cyclopentane, 1,3-dimethyl-2-(1-methylethylidene)	6.63	483.808	9.9
Cyclohexanone, 2-ethyl-2-propyl	6.693	19.0575	10
Cyclohexanone, 2-ethyl-2-propyl	6.777	8.6005	10
1,3-cyclohexadiene, 1,3,5,5-tetramethyl	6.837	228.932	9.8
4-heptanone, 2-methyl	7.104	256.694	7
1,4-cyclohexadiene, 3,3,6,6-tetramethyl	7.296	31.1503	9.8
Cyclohexene, 1,5,5-trimethyl-3-methylene	7.457	211.607	9.8
6-methyl 2-heptanone	7.746	112.178	7
Benzene 1-methylethyl	7.837	45.4742	9
Mesitylene	7.945	2706.33	9
Cyclohexane, 1-methyl-3-(1-methylethylidene)	8.376	101.178	9.9
Benzene 1-methyl-3-propyl	9.184	335.165	10
Benzene 1-ethyl-2,4-dimethyl	9.539	174.585	10
4,4-dimethyl-2-propenylcyclopentanone	9.625	112.764	9
3,5-decadiene, 2,2-dimethyl-,(Z,Z)-	9.739	129.16	11.8
Benzene, 1-methyl-4-(2-methylpropyl)-	9.824	314.579	11
Benzene, 1-methyl-4-(1-methylpropyl)-	10.337	527.378	11
3,5-xylenol	10.6	489.437	7.4
Benzene 1,4-dimethyl-2-(2-methylpropyl)	10.834	225.625	12
Phenol 2-ethyl-5-methyl	11.248	140.273	8.4
Phenol 2,4,6-trimethyl	11.644	377.404	8.4
Phenol, 2-ethyl-4,5-dimethyl	12.201	783.784	9.4
Benzene, 1,3-dimethyl-2-propoxy	12.762	161.957	10

Phenol, 2-(1,1-dimethylethyl)-3-methyl-	12.908	198.823	10.4
1,1,6,8-tetramethyl-1,2-dihydronaphthalene	13.036	161.097	14
2,5,8-trimethyltetralin	13.216	148.208	13
Propofol	13.264	106.85	11.4
Naphthalene, 1,2,3,4-tetrahydro-2,2,5,7-tetramethyl	13.34	241.613	14
1,1,4,5,6-pentamethyl-2,3-dihydro-1H-indene	13.444	432.647	14
1,1,4,5,6-pentamethyl-2,3-dihydro-1H-indene	13.55	180.301	14
1,1,5,6-tetramethyl-1,2-dihydronaphthalene	13.633	210.419	14
1,3-benzodioxole, 5-(2,2-dimethylethyl)	13.725	100.236	8
Naphthalene, 2,3,6-trimethyl	13.944	294.189	13
1H-2-indenone, 2,4,5,6,7,7a-hexahydro-3-(1-methylethyl-7a-methyl	14.033	92.1662	12
2-methoxy, 4-methyl, 1-pentylbenzene	14.207	88.2977	12
5H-benzocycloheptene, 6,7-dihydro-3,5,5,9-tetramethyl	14.245	72.1027	15
1.4.5.8-tetramethyl naphthalene	15.182	228.777	14

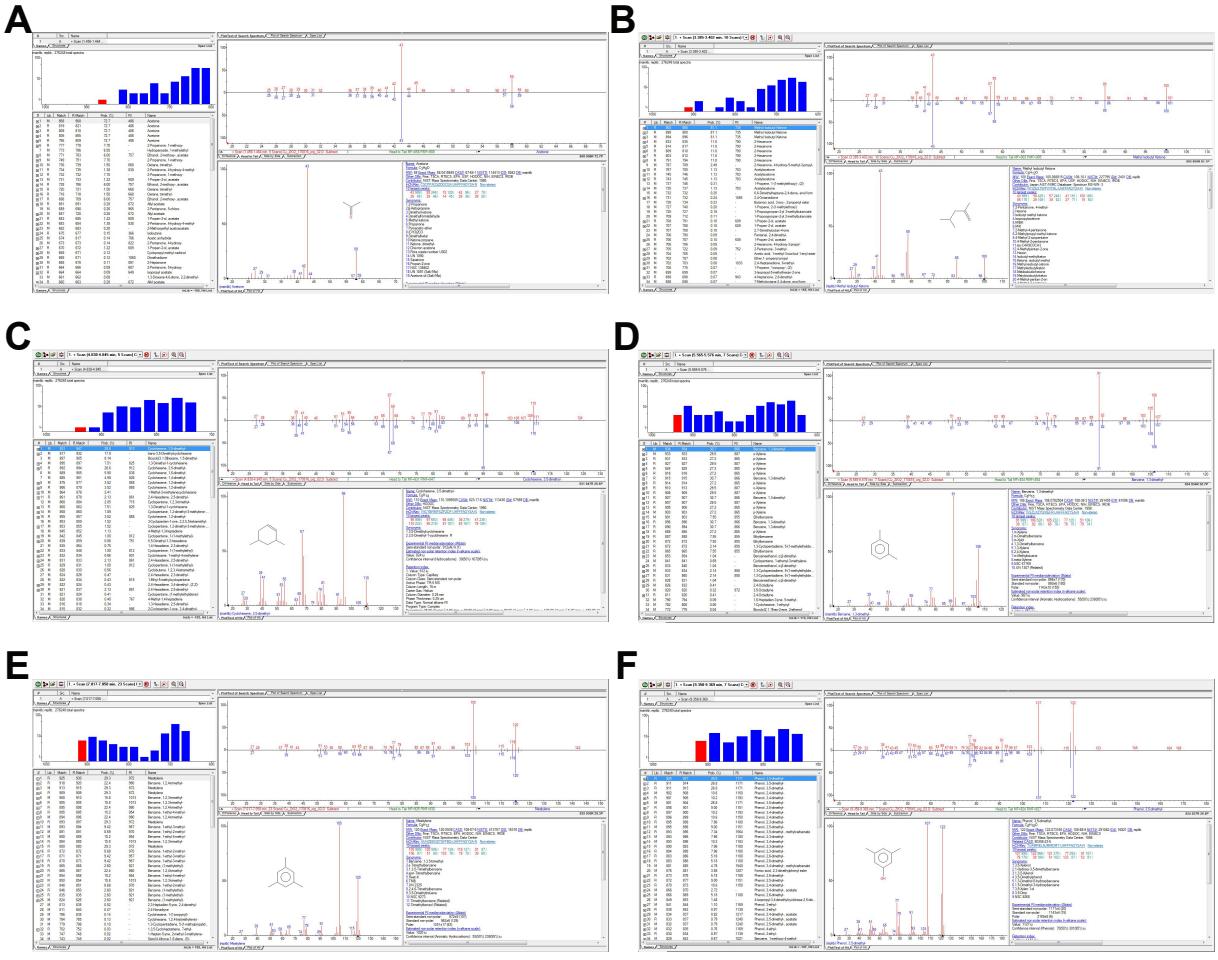

Fig. S3 Selected mass spectra for major product peaks from Fig. S2. A) Acetone, B) MIBK, C) Cyclohexene, 3,5-dimethyl, D) m-xylene, E) Mesitylene and F) 3,5-xylenol. The product spectrum is in red while the reference spectrum from the NIST database is in blue.

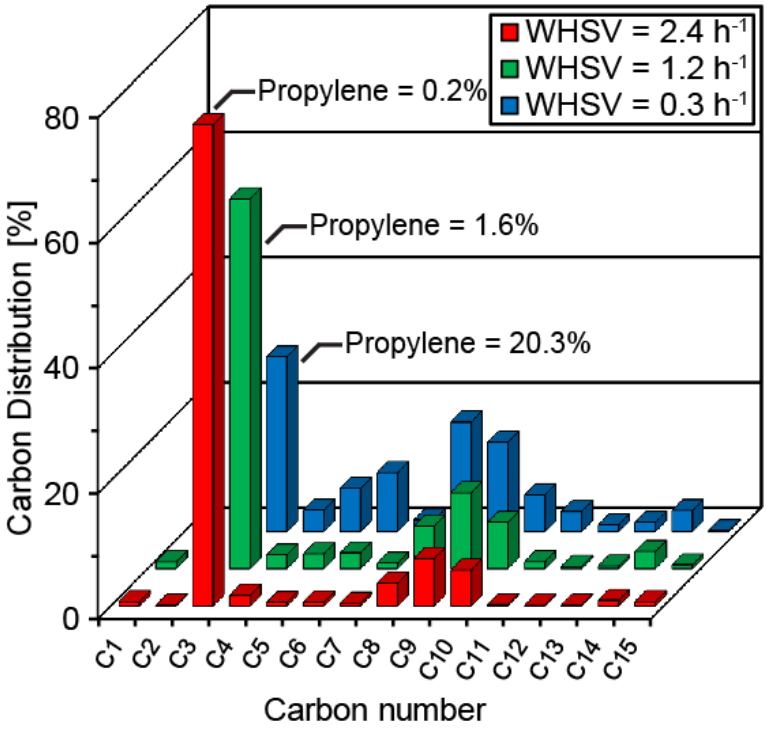

Fig. S4 Molar carbon distribution of the product stream during the upgrading of pure acetic acid over 2g 2 wt% Cu/ZrO_2 at different WHSV (T = 400 °C, P = 10 bar H_2, H_2 flow = 20 mL/min). The C_3 fraction was almost exclusively acetone with a very small fraction of propylene. This molar carbon fraction of propylene is given explicitly for each WHSV.

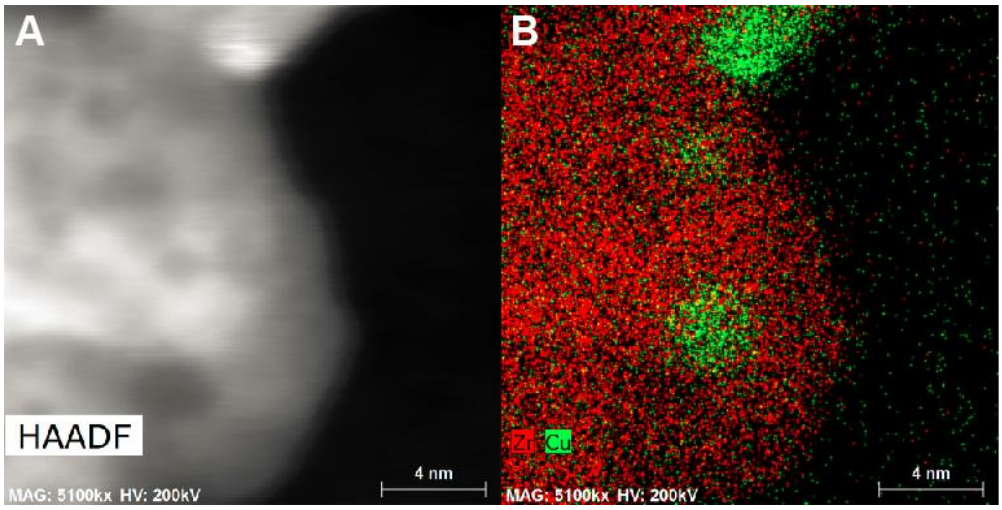

Fig. S5 A) HAADF-STEM image and B) EDX mapping of fresh 2 wt% Cu/ZrO_2 catalyst.

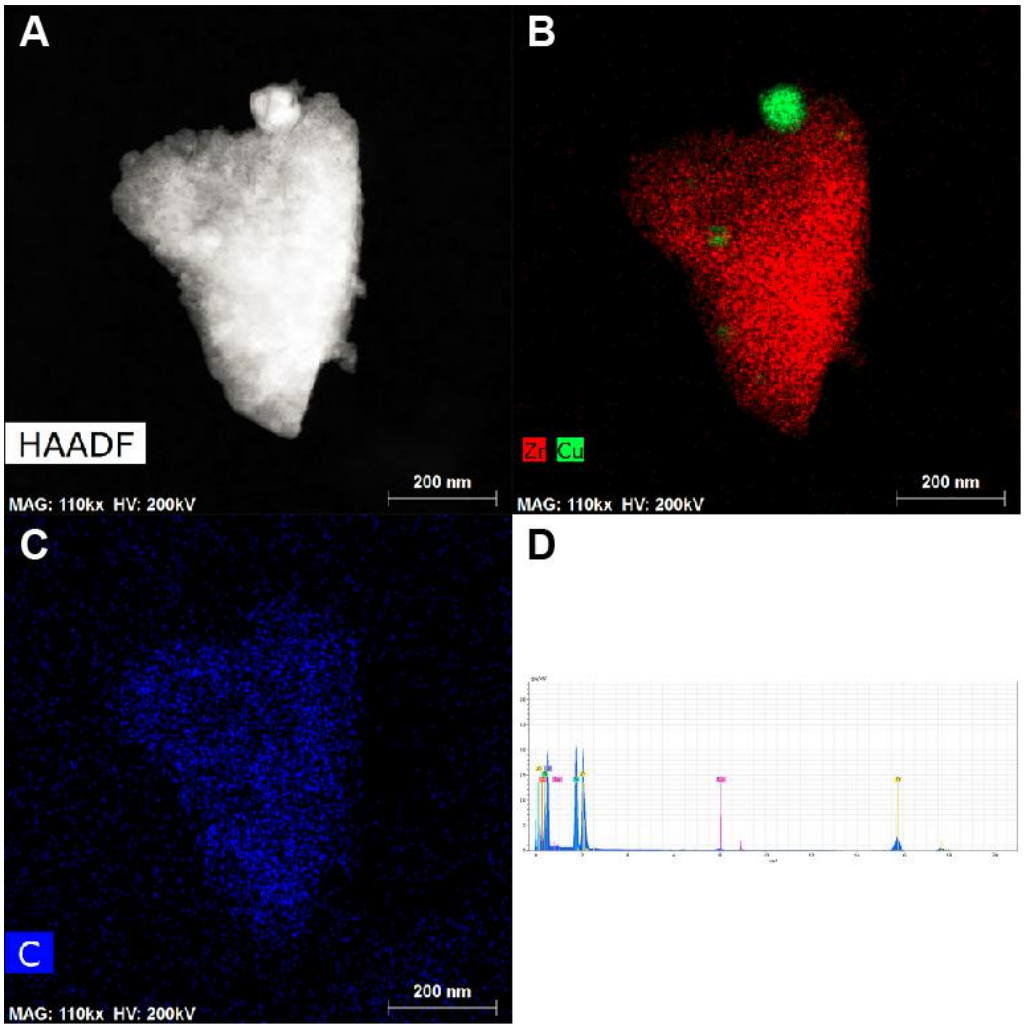

Fig. S6 A) HAADF-STEM image, B), C) EDX mapping and D) EDX spectra of spent 2 wt% Cu/ZrO_2 catalyst on a SiN grid.

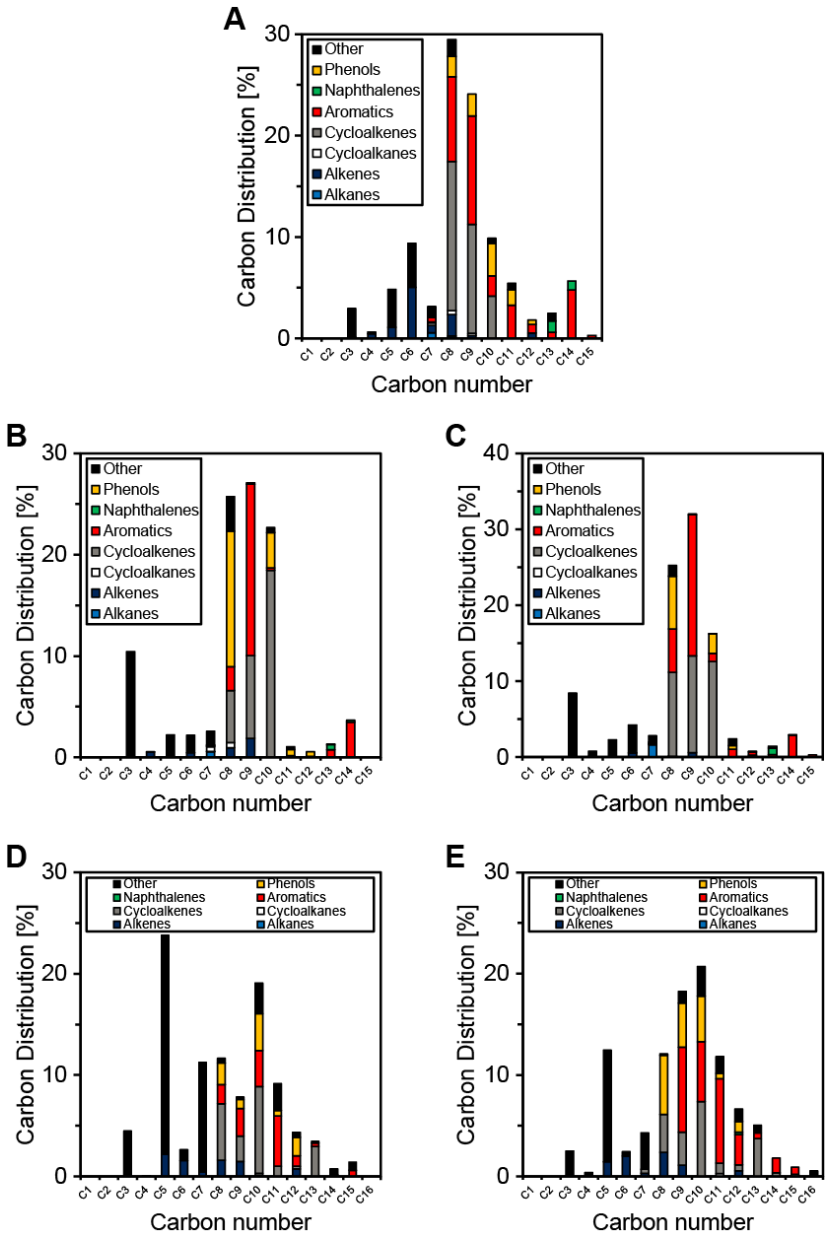

Fig. S7 Molar carbon distribution of the organic oil during the upgrading of: A) Pure acetic acid (time on stream = 21.3 h, corresponding to Fig. 3D), B) 50 wt% aqueous acetic acid (time on stream = 265.3 h, corresponding to Fig. 4C), C) 40.3 wt% biomass-derived acetic acid (time on stream = 76.3 h, corresponding to Fig. 4C), D) 28/12 wt% aqueous acetic/butanoic acid (time on stream = 72.1 h, corresponding to Fig. 5C) and E) 28/12 wt% biomass-derived acetic/butanoic acid (time on stream = 66.2 h, corresponding to Fig. 5C) (T = 400 °C, P = 10 bar H_2, H_2 flow = 20 mL/min). "Others" consisted of oxygenates that are not phenols.

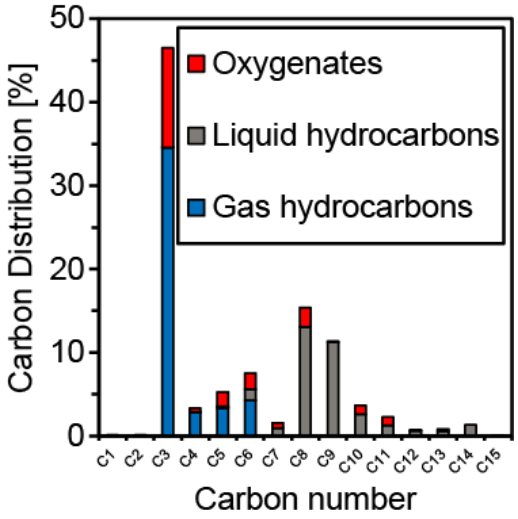

Fig. S8 Molar carbon distribution of the product stream during the upgrading of 50 wt% aqueous acetic acid over 2g of 2 wt% Cu/ZrO_2 (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1}, H_2 flow = 20 mL/min, conversion of acetone = 87.8 %, time on stream = 61.4 h). Oxygenates refers to oxygenated molecules in organic, aqueous and gas phases.

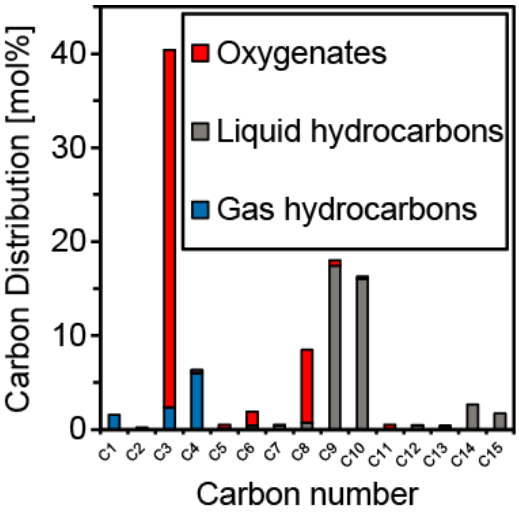

Fig. S9 Molar carbon distribution of the product stream during the upgrading of pure acetic acid over 2g of 2 wt% Cu/ZrO_2 at 1 bar H_2 partial pressure (T = 400 °C, P = 10 bar 10 % H_2 in argon, WHSV = 0.3 h^{-1}, 10 % H_2 in argon flow = 20 mL/min, conversion of acetone = 70.6 %, time on stream = 34.3 h). Oxygenates refers to oxygenated molecules in organic, aqueous and gas phases.

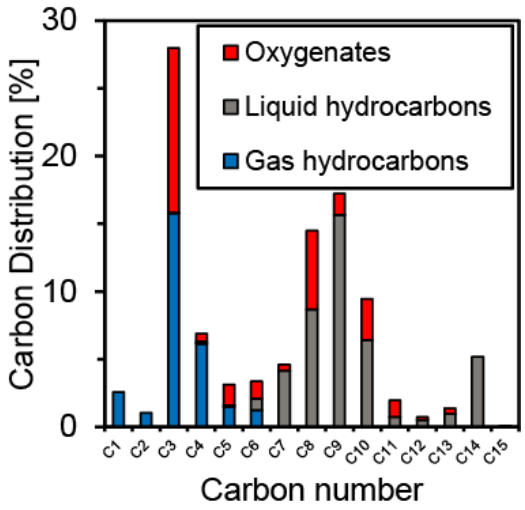

Fig. S10 Molar carbon distribution of the product stream during the upgrading of pure acetic acid over 2g of 0.5 wt% Cu/ZrO_2 (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1}, H_2 flow = 20 mL/min, conversion of acetone = 91.2 %, time on stream = 42.7 h). Oxygenates refers to oxygenated molecules in organic, aqueous and gas phases.

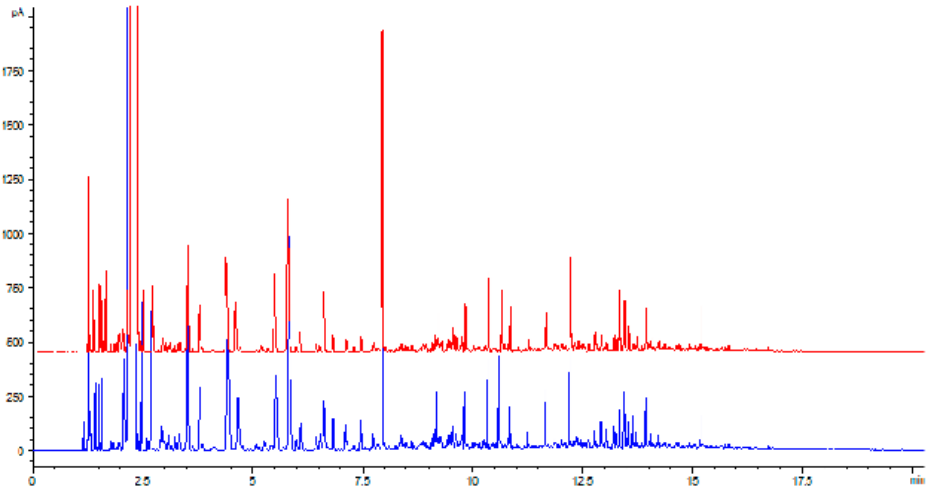

Fig. S11 Overlaid gas chromatograms of the organic oil during the upgrading of pure acetic acid. The blue chromatogram corresponds to the small scale 2g 2 wt% Cu/ZrO_2 catalyst at H_2 flow = 20 mL/min, time on stream = 21.3 h, which was shown above as Fig. S2 and corresponds to Fig. 3D. The red chromatogram corresponds to the upscaled 20g 2 wt% Cu/ZrO_2 catalyst at H_2 flow = 200 mL/min, time on stream = 6.6 h. (T = 400 °C, P = 10 bar H_2, WHSV = 0.3 h^{-1})

Fig. S12 Biofilm membrane reactor used to produce butanoic acid from pretreated beech wood.