Electronic Supplementary Material (ESI) for Green Chemistry.

Fuel and chemicals from wet lignocellulosic biomass waste streams by hydrothermal carbonization

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Supplementary Information

For the pilot plant trials four biomass feedstocks were chosen: two different types of organic fraction of municipal solid (OFMSW-1 and OFMSW-2), orange peel waste (OPW) and the residues of a pepper plantation (PEP). The first type of OFMSW, i.e. OFMSW-1, was obtained separation from integrated collection of MSW (Figure S1). Several reasons support the use of this material as raw material for the HTC process although a biological stabilization process has been applied prior to the separation of the inorganics. The use of this material as compost is not realistic due to its quality and low market demand. On the other hand it is very suitable for the HTC process due to its chemical composition and the physical nature (particle size, humidity, etc.) and its concentration at one place avoiding transportation costs.

Figure S1. Biomass feedstock OFMSW-1 as received at the plant.

As second raw material for the HTC trial the OFMSW (OFMSW-2) from separate collection was processed (Figure S2). On medium term, this should be the predominate biowaste from households in Europe, together with garden prunings. Furthermore, the worst case with respect to inorganic contamination (stones, metals, plastics, etc.; cf. Figure S3) was adopted with the aim to evaluate robustness of process and plant. The ash content of the biomass was 25% whereas statistics show that, in general, this value is below 10% and values below 5% are also realistic.

Figure S2. Biomass OFMSW-2 as received at the plant

Figure S3. Inorganic material separated at different stages of the HTC process.

OPW and PEP feedstocks were received from local industry. OPW was produced during orange juice production. The PEP material is the residue from a pepper plantation.

Figure S 4. OPW (left hand side) and PEP (right hand side) feedstocks.

Ash-composition of hydrochar

Table S1. Ash composition (ash determination at 815 ºC).

	Na_2O [%]	K_2O [%]	MgO [%]	CaO [%]	Al_2O_3 [%]	Fe_2O_3 [%]	P_2O_5 [%]
OFMSW-1	1.4	3.1	4.1	36.9	11.1	4.4	6.7
OFMSW-2	1.8	3.4	3.1	33.4	7.7	3.8	6.8
OPW	2.0	3.3	4.0	36.4	7.5	5.1	13.6
PEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not determined.

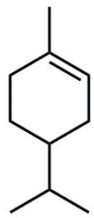
Table S2. Heavy metal content of the produced hydrochar samples.

	As [ppm]	Cd [ppm]	Cr [ppm]	Co [ppm]	Cu [ppm]	Pb [ppm]	Mo [ppm]	Ni [ppm]	Se [ppm]	Zn [ppm]	B [ppm]
OFMSW-1	195	89	322	238	1610	330	453	189	205	2320	3050
OFMSW-2	157	138	235	240	435	208	245	150	145	1160	3610
OPW	63	2.9	162	1260	531	235	38	108	51	1010	787
PEP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

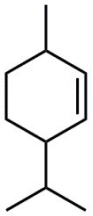
n.d.: not determined.

Up-grading of the monoterpene mixture

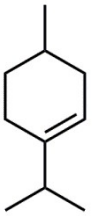
Table S3. Conversions of the monoterpene mixture and product distribution for the dehydrogenation experiments with different catalysts at 320 ºC (1 = *para*-cymene).



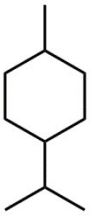
1-*p*-menthene
1a



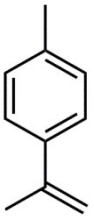
2-*p*-menthene
1b



3-*p*-menthene
1c



p-menthane
1d



p-cymenene
1e

					Yield					
	Time		Carrier	Conv.	**1**	**1a**	**1b**	**1c**	**1d**	**1e**
Entry	[h]	Catalyst	gas	[%]	[%]	[%]	[%]	[%]	[%]	[%]
1	1	Pd/C	N_2	100.0	98.2	0.5	0.1	0.9	0.0	0.3
2	15	Pd/C	N_2	57.3	45.2	4.1	0.6	4.2	0.0	3.2
3	1	Pd/Al_2O_3	N_2	100.0	93.4	1.3	0.3	2.4	0.0	2.6
4	7	Pd/Al_2O_3	N_2	30.4	24.6	0.8	0.6	1.2	0.0	3.2
5	1	Pd/C	H_2	100.0	89.3	2.3	0.3	4.3	3.7	0.0
6	14	Pd/C	H_2	100.0	67.2	10.1	1.5	19.9	1.3	0.0