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Supplementary Information for: Integrating anaerobic digestion and slow pyrolysis improves the product portfolio of a cocoa waste biorefinery

Stef Ghysels[b,c,a], Nayaret Acosta[b,a], Adriana Estrada[b], Mehmet Pala[b], Jo De Vrieze[c], Frederik Ronsse[b], Korneel Rabaey[c,*]

[a] *These authors contributed equally*
[b] *Thermochemical Conversion of Biomass Research Group, Department of Green Chemistry and Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium.*
[c] *Centre for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, B-9000 Gent, Belgium*

[*] Korneel.Rabaey@UGent.be

Appendix A. Calibration of GC-MS detected compounds

The GC-MS was calibrated with a set of reference compounds typically found in pyrolysis liquids, which were quantified directly. Chemical compounds for which the GC-MS was not calibrated were quantified by using the response factors from calibrated compounds having structural similarity or which belong to the same chemical group (Mohabeer et al., 2017).

Table A.1: Classification of the quantified chemical compounds in the pyrolysis liquids according to their chemical group and indication of the applied response factors used for quantification of the chemical compounds. RT: retention time (minutes).

Chemical group	Compounds in the chemical group quantified with this response factor	RT in minutes	Reference compound for calibration	Resonse factor of reference compound
Light oxygenates	Acetic acid	9.10	Acetic acid	0.41
	Butanoic acid	20.96		
	Propanoic acid	12.20		
	1-Hydroxy-2-propanone	10.24	1-Hydroxy-2-propanone	0.44
	2-Furanmethanol	17.23	Furfural	0.61
	4-Hydroxybutanoic acid	21.04	3-Methyl-1,2-cyclopentanedione	0.67
2-Cyclopenten-1-one derivates	2-Cyclopenten-1-one, 2-methyl- 2-Cyclopenten-1-one, 3-methyl- 2-Cyclopenten-1-one, 3-(1-methylethyl)-	20.8; 17.62; 24.25	3-Methyl-1,2-cyclopentanedione	0.67
	2-Cyclopenten-1-one, 2,3-dimethyl- 2-Cyclopenten-1-one, 3,4-dimethyl-	21.21; 22.54		
	2-Cyclopenten-1-one, 2,3,4-trimethyl-	22.79		
Phenol	Phenol	23.41	Phenol	1.74
Alkyl phenols	Phenol, 4-ethyl- Phenol, 3-ethyl- Phenol, 2-ethyl-	27.08; 28.33; 28.39	Phenol	1.74
	Phenol, 4-methyl- Phenol, 3-methyl- Phenol, 2-methyl-	24.83; 24.92; 25.86		
	Phenol, 2,6-dimethyl- Phenol, 2,5-dimethyl- Phenol, 2,3-dimethyl- Phenol,3,4-dimethyl-	27,21; 28,24; 29,06;		
	Phenol, 2-ethyl-6-methyl- Phenol, 2-ethyl-5-methyl Phenol, 2-ethyl-4-metyl	29.15; 29.53		
	Phenol, 2,4,6-trimethyl-	30.41		
	Phenol, 4-propyl-	30.67		
Methoxy phenols	2-Methoxyphenol	24.00	2-Methoxyphenol	1.49
	2,6-Dimethoxyphenol	32.20		
Methoxyalkyl phenols	Phenol, 4-ethyl-2-methoxy-	29.29	2-Methoxy-4-methyl phenol	1.53
	Phenol, 2-methoxy-4-propyl-	31.53		
	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	30.26		
	2-Methoxy-4-vinylphenol	30.86		

	Phenol, 2-methoxy-4-methyl-	27.00		
	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	34.23		
Substituted benzenes	1,2,4-Trimethoxybenzene	34.51	2-Methoxyphenol	1.49
	Benzenepropanenitrile	30.16	Phenol	1.74
	Indole	32.42	Naphtalene	2.19
lipid derivatives	3-Nonen-2-ol, (E)-	25.38	Ethylene glycol	0.53
	Overlapping peaks, mostly Tridecanoic acid, methyl ester; Methyl tetradecanoate	42-47		
	Tetradecane	30.85		
	Hexadecane	33.24	Benzene	2.25
	Pentadecane	35.52		

Appendix B. Composition of cocoa pods aqueous phase pyrolysis liquids

The composition of the aquous phase from pyroysis of raw coco pod husks is shown in Figure B.1.

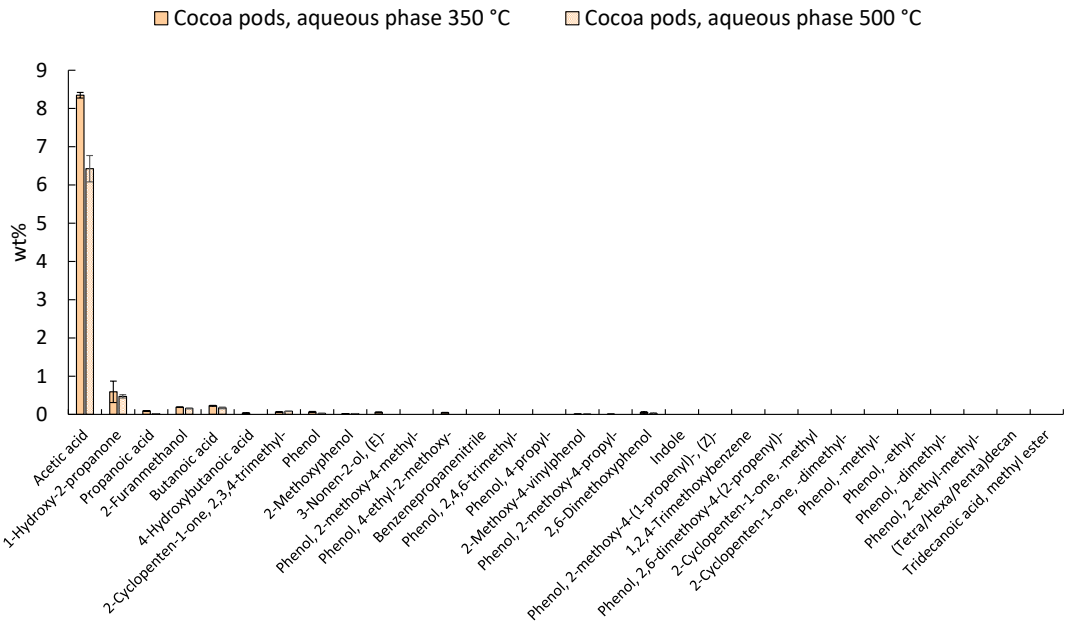

Figure B.1: Composition of the aqueous phase pyrolysis liquids in wt.% on liquid-basis, determined through GC-MS analysis.

Appendix C. Detailed composition of all organic phase pyrolysis liquids

The concentration of individual compounds present in all organic phase pyrolysis liquids is shown in Figure C.2.

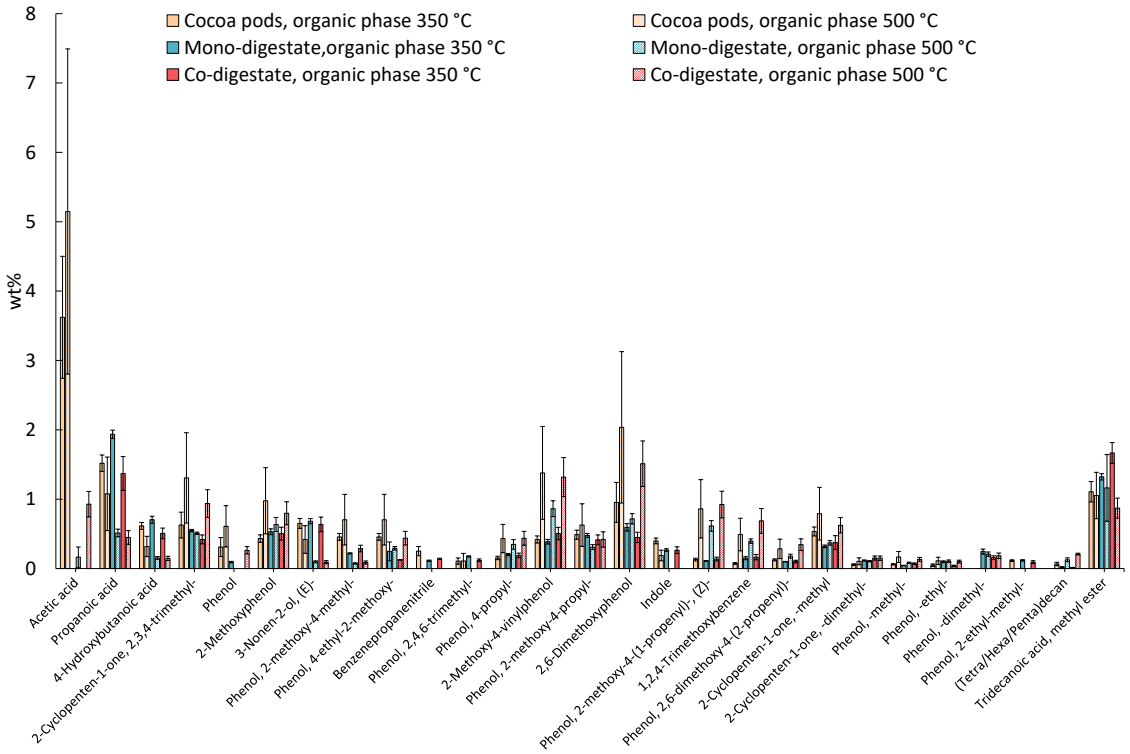

Figure C.2: Individual compounds in pyrolysis liquids in wt.% on liquid-basis, determined through GC-MS analysis.

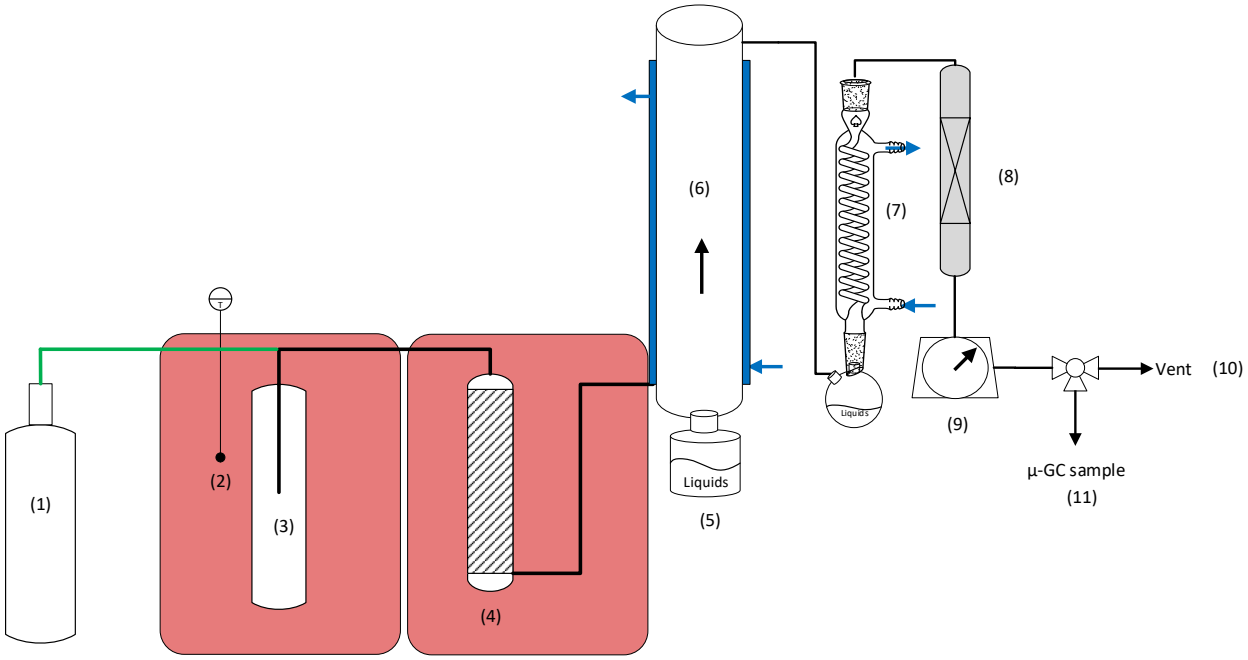

Figure D.3: Scheme of the pyrolysis setup: (1) nitrogen tank; (2) thermocouples; (3) fixed-bed reactor vessel; (4) knock-out vessel; (5) liquid collection vessel; (6) electrostatic precipitator (ESP); (7) glass condenser; (8) cotton wool filter; (9) gas meter; (10) exhaust system and (11) μ-GC sample line.

Appendix D. Pyrolysis set-up

References

Mohabeer, C., Abdelouahed, L., Marcotte, S., Taouk, B., 2017. Comparative analysis of pyrolytic liquid products of beech wood, flax shives and woody biomass components. Journal of Analytical and Applied Pyrolysis 127, 269 – 277. doi:https://doi.org/10.1016/j.jaap.2017.07.025.