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Supplementary Materials

Py-GC-MS Study on Catalytic Pyrolysis of Biocrude Obtained via HTL of Fruit Pomace

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Table S1. The mass of solid residue and share of identified products evolved after thermal and catalytic decomposition of the studied HTL biocrude.

Name	Pyrolysis 500 °C, 50 °C s^{-1}					
	No Catalyst (Thermal)		ZSM-5		HY	
Share of total peak area of identified compounds on GC-MS chromatogram ($S_{identif}$)	**85.9%**	**±5.1%**	89.9%	±4.0%	96.0%	±0.9%
Mass of solid residue in pyrolyzer (wt%) ($m_{residue}$)	27.8%	±5.6%	23.5%	±3.5%	26.3%	±5.1%

Table S2. Comparison between the relative and estimated real share of group composition of the fractions evolved after thermal (500 °C) and catalytic pyrolysis of the studied HTL biocrude.

Group Name	Relative Share Regarding to the Compounds Identified from GC-MS Analysis			Share Regarding to the Sample Subjected to Test (wt%)		
	No Catalyst (Thermal)	ZSM-5	HY	No Catalyst (Thermal)	ZSM-5	HY
Aliphatic HC (unsaturated)	10.76%	32.81%	33.40%	6.67%	22.57%	23.61%
Aliphatic HC (saturated)	—	0.73%	2.11%	—	0.50%	1.49%
Cyclic HC	5.72%	12.41%	12.89%	3.55%	8.54%	9.11%
Aromatic HC	12.63%	23.26%	25.76%	7.84%	16.00%	18.21%
Carboxylic acids	19.27%	7.75%	1.07%	11.96%	5.33%	0.76%
Esters	22.63%	13.43%	8.91%	14.04%	9.24%	6.30%
Alcohols, ketones, aldehydes	12.18%	6.38%	8.77%	7.56%	4.39%	6.20%
Phenol deriv.	6.49%	0.62%	1.65%	4.03%	0.42%	1.17%
N-compounds	9.53%	0.81%	3.18%	5.91%	0.55%	2.25%
CO_2	0.80%	1.87%	2.27%	0.49%	1.29%	1.60%

Table S3. Identified volatile products evolved during thermal and catalytic pyrolysis of biocrude from blackcurrant pomace at 500 °C determined by Py-GC-MS.

Group	RT (min)	Compound Name	Pyrolysis 500 °C		
			No Catalyst (Thermal)	ZSM-5	Zeolite HY
CO_2	**3.0**	Carbon dioxide	0.80%	1.87%	2.27%
Aliphatic HC (unsaturated)	3.1	Propene	1.90%	10.67%	7.20%
	3.2	1-Propene, 2-methyl-	2.46%	7.15%	4.56%
	3.6	2-Pentene	3.22%	4.65%	4.25%
	3.7	2-Butene, 2-methyl-	0.30%	0.79%	2.25%
	4.3	1-Pentene, 2-methyl-	—	—	1.56%
	4.5	2-Hexene-	1.11%	2.01%	3.77%
	5.2	1,3,5-Hexatriene, (Z)-	0.05%	1.06%	0.87%
	5.6	4-Methyl-2-pentyne	0.26%	0.26%	0.56%
	6.0	2,4-Hexadiene	0.09%	0.06%	1.03%
	4.7	2-Pentene, 3-methyl-	—	0.07%	0.16%
	6.5	(Z)-2-Heptene	0.76%	0.81%	—
	6.6	1,4-Pentadiene, 3,3-dimethyl-	—	1.18%	0.90%
	7.0	2-Heptene	—	0.28%	0.20%
	7.4	3-Heptyne	—	—	0.16%
	8.7	2,3-Hexadiene, 2-methyl-	—	0.86%	0.97%
	10.3	1-Octene	0.60%	0.72%	1.02%
	10.6	4-Octene, (E)-	—	0.11%	0.61%
	11.4	3-Octene, (Z)-	—	0.25%	0.28%
	13.8	1-Nonyne	—	0.07%	0.08%
	15.5	4-Nonene	—	0.68%	0.74%
	20.0	5-Decene, (E)-	—	—	0.98%
	20.5	5-Decene	—	0.22%	0.11%
	24.5	4-Octene, 2,3,6-trimethyl-	—	0.24%	0.28%
	27.8	4-Undecene, 5-methyl-	—	0.38%	0.63%
	31.4	2-Dodecene, 2-methyl-	—	—	0.16%
	37.8	1-Tridecene	—	—	0.15%
	55.2	4-Hexadecen-6-yne, (Z)-	—	0.08%	—
Aliphatic HC (saturated)	6.5	Heptane	—	—	0.69%
	15.6	Nonan	—	0.73%	1.01%
	38.0	Undecane, 4,7-dimethyl-	—	—	0.24%
	72.4	Hexadecane	—	—	0.17%
Cyclic HC	3.8	Cyclopropane, methylmethylene-	0.08%	0.61%	0.78%
	3.9	Cyclopentene	0.10%	0.42%	0.69%
	4.8	Cyclopentene, 3-methyl-	0.92%	0.27%	—
	5.1	3-Vinyl-1-cyclobutene	0.16%	0.74%	0.88%
	5.3	Cyclopentene, 1-methyl-	0.16%	0.81%	2.11%
	6.2	Cyclopentane, 1,2-dimethyl-	0.63%	0.62%	1.17%
	7.6	Cyclopropane, trimethylmethylene-	0.00%	0.17%	0.00%
	8.5	1,3-Cycloheptadiene	—	—	0.14%
	9.6	3-Methylenecyclohexene	—	2.14%	0.93%
	10.7	Cyclopentane, 1,2,4-trimethyl-	0.48%	1.81%	0.16%
	11.2	Cyclohexene, 3-ethyl-	—	0.41%	0.25%
	12.4	Cyclohexane,ethenylidene-	—	0.26%	0.11%
	12.6	1,3-Cyclohexadiene, 5-ethyl-	—	0.23%	0.37%
	12.9	Cyclopentadiene, 2,5,5-trimethyl-	—	0.73%	0.26%
	13.0	1-(2-Propenyl)cyclopentene	—	0.66%	0.38%
	13.4	Cyclohexane, ethylidene-	—	0.20%	0.64%
	16.1	Cyclopentane, ethylidene-	—	0.23%	—
	16.5	Tricyclo(4.2.2.0(1,5))decane	—	—	0.06%

	16.8	Cyclohexene,1-propyl-	—	—	0.15%
	17.8	Cyclopentene, 1-butyl-	—	0.29%	0.63%
	21.6	Limonene	2.62%	1.69%	2.83%
	23.5	2,2-Dimethyl-3-vinyl-bicyclo(2.2.1)heptane	—	0.12%	0.18%
	54.7	Cyclohexane, 1,2,3,5-tetraisopropyl-	0.50%	—	0.13%
Aromatic HC	5.5	Benzene	—	0.68%	0.47%
	9.2	Toluene	2.78%	4.13%	5.43%
	13.7	Ethylbenzene	—	1.43%	1.72%
	14.2	Xylenes	—	2.84%	4.31%
	18.1	Benzene, propyl-	—	1.09%	0.99%
	18.6	Benzene, 1-ethyl-4-methyl-	—	1.90%	1.99%
	18.9	Benzene, 1,2,3-trimethyl-	—	—	0.13%
	19.3	Benzene, 1-ethyl-2-methyl-	—	—	0.05%
	22.2	Indene	—	0.80%	1.00%
	22.6	Benzene, n-butyl-	—	—	0.71%
	23.1	Benzene, 1-methyl-4-propyl-	—	—	0.23%
	25.4	Benzene, 4-ethenyl-1,2-dimethyl-	—	0.37%	0.03%
	26.2	Benzene, 1-methyl-4-(1-methylpropyl)-	—	0.16%	0.07%
	26.0	Methano-indene, -tetrahydro-	—	0.36%	0.52%
	26.4	2-Methylindene	—	0.42%	1.95%
	26.6	Benzene, pentyl-	—	1.17%	1.70%
	27.8	Naphthalene	—	0.11%	1.30%
	29.4	Benzothiazole	—	—	0.05%
	30.4	Benzene, hexyl-	—	0.49%	0.51%
	30.8	1H-Indene, 1,1-dimethyl-	—	—	0.21%
	32.3	Naphthalene, 2-methyl-	—	—	0.40%
	31.7	1H-Indene, 1-ethylidene-	—	—	0.18%
	33.9	Benzene, heptyl-	—	0.47%	0.46%
	35.8	Naphthalene, 1,2-dimethyl-	—	—	0.18%
	36.1	Benzene, 1-pentyl-4-vinyl-	—	—	0.18%
	44.1	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-	3.05%	3.92%	0.44%
	47.2	Benzene, 1,1'-(2-butene-1,4-diyl)bis-	—	0.05%	—
	48.9	2,5-Diphenyl-1,5-hexadiene	0.96%	0.56%	0.03%
	50.9	1H-Indene, 1-(phenylmethylene)-	0.37%	—	—
	51.2	1-(4-Methylphenyl)-4-phenylbuta-1,3-diene	0.38%	0.06%	—
	61.1	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)-	5.08%	2.26%	0.50%
Carboxylic acids	4.3	Acetic acid	2.55%	—	—
	8.2	6-Nonynoic acid	0.29%	—	—
	15.7	8-Nonynoic acid	1.05%	—	—
	18.9	Undec-10-ynoic acid	0.06%	—	—
	34.7	trans-Traumatic acid	—	0.36%	0.78%
	50.4	n-Hexadecanoic acid	3.15%	1.44%	—
	52.0	9-Hexadecenoic acid	—	—	0.04%
	54.5	Linoelaidic acid	12.22%	4.73%	0.25%
	54.6	Oleic Acid	2.28%	1.00%	—
	55.0	Octadecanoic acid	0.10%	—	—
	56.0	Gamolenic acid	—	0.18%	—
	59.8	cis-13-Eicosenoic acid	0.12%	—	—
Esters	4.7	Methoxyacetic acid, methyl ester	0.05%	—	—
	13.7	(S)-Isopropyl lactate	0.40%	—	—
	14.1	8-Nonynoic acid, methyl ester	0.08%	—	—
	15.2	Hexanoic acid, 2-phenylethyl ester	0.96%	1.10%	1.63%
	15.4	3-Cyclopentylpropionic acid, 2-phenylethyl ester	—	0.19%	—

	21.8	Acetic acid, 2-methylene-bicyclo(3.2.1)oct-6-en-8-yl ester	—	0.78%	—
	24.4	Pentanoic acid, 4-oxo-, 1-methylethyl ester	1.18%	—	0.62%
	25.3	Cyclopentanecarboxylic acid, 2-hydroxy-1-(2-propenyl)-, methyl ester, cis-	0.06%	—	0.08%
	29.4	Acetic acid, 7-hydroxy-1,3,4,5,6,7-hexahydro-2H-naphthalen-4a-ylmethyl ester	—	—	0.05%
	30.1	Succinic acid, non-5-yn-3-yl propyl ester	0.10%	—	0.42%
	~33.0	2,5-Octadecadiynoic acid, methyl ester	0.38%	2.98%	2.86%
	43.5	5-Benzofuranacetic acid, 6-ethenyl-2,4,5,6,7,7a-hexahydro-3,6-dimethyl-.alpha.-methylene-2-oxo-, methyl ester	1.62%	0.47%	—
	49.1	Propanoic acid, 2-methyl-, (dodecahydro-6a-hydroxy-9a-methyl-3-methylene-2,9-dioxoazuleno[4,5-b)furan-6-yl)methyl ester	0.08%	0.04%	—
	49.5	5,8,11-Heptadecatriynoic acid, methyl ester	0.40%	0.22%	—
	51.8	Isopropyl palmitate	3.63%	1.65%	0.62%
	52.0	7-Methyl-Z-tetradecen-1-ol acetate	1.08%	—	—
	53.5	9,12-Octadecadienoic acid, methyl ester	1.58%	0.12%	—
	53.6	9-Octadecenoic acid (Z)-, methyl ester	0.25%	—	—
	54.0	Succinic acid, 3-methylbut-2-en-1-yl diphenyl-methyl ester	0.11%	—	—
	55.3	9,12,15-Octadecatrienoic acid, 2,3-dihydroxy-propyl ester	0.21%	0.16%	—
	55.6	Isopropyl linoleate	7.50%	4.45%	0.98%
	55.7	Elaidic acid, isopropyl ester	2.43%	—	0.04%
	55.9	cis-9-Octadecenoic acid, propyl ester	—	0.77%	0.78%
	56.3	Isopropyl stearate	0.15%	0.22%	—
	56.7	11,13-Dimethyl-12-tetradecen-1-ol acetate	0.30%	0.16%	—
	57.6	trans,trans-9,12-Octadecadienoic acid, propyl ester	0.09%	0.11%	—
	87.8	Octadecanoic acid, octadecyl ester	—	—	0.76%
Alcohols, ketones, aldehydes	6.7	Furan, 2,5-dimethyl-	0.62%	—	—
	7.1	2,4-Hexadien-1-ol	0.16%	0.81%	0.46%
	7.7	1-Butanol, 2-methyl-	0.13%	—	0.02%
	7.8	2-Hydroxymethylcyclopentanol (trans)	0.29%	—	0.03%
	9.8	3-Cyclohexene-1-methanol	0.05%	0.10%	0.09%
	10.9	Bicyclo[2.2.1]hept-2-en-7-ol	—	0.25%	0.29%
	11.0	1-Cyclohexene-1-methanol	0.08%	0.52%	0.22%
	11.5	2-Octyn-1-ol	0.18%	—	—
	12.8	2,4-Pentadien-1-ol, 3-pentyl-, (2Z)-	—	—	0.21%
	13.4	1-Methoxymethoxy-hexa-2,4-diene	0.03%	—	—
	15.6	1-Octyn-3-ol, 4-ethyl-	0.31%	—	—
	15.8	2-Cyclopenten-1-one, 2-methyl-	0.70%	—	—
	15.9	cis,cis-4,6-Octadienol	—	—	—
	16.3	Cyclohexanol, 2-methylene-6-methyl-	—	—	0.26%
	16.6	Campholenal	—	0.17%	0.05%
	17.2	Cyclohexaneethanol, 2-methylene-	0.08%	0.56%	0.46%
	18.1	3-Cyclohexene-1-propanal	0.11%	0.05%	0.05%
	18.8	Cyclopentanol, 1-(1-methylene-2-propenyl)-	0.51%	—	0.15%
	19.6	7-Oxabicyclo[4.1.0]heptane, 3-oxiranyl-	—	0.41%	0.11%
	20.2	3-Cyclohexene-1-propanal	—	0.58%	1.31%
	20.8	Verbenol	0.42%	0.17%	0.94%
	21.2	cis-Verbenol	0.57%	0.18%	0.60%
	21.4	Benzeneethanol, .beta.-ethenyl-.alpha.-phenyl-	—	—	0.35%
	22.0	5,7-Octadien-3-ol, 2,4,4,7-tetramethyl-, (E)-	0.11%	—	—

	22.5	cis-(-)-1,2-Epoxy-p-menth-8-ene	0.07%	—	0.14%
	23.8	(1R)-(-)-Myrtenal	—	0.38%	0.56%
	24.0	2-Nonenal, (E)-	—	—	0.32%
	24.2	2-Cyclopenten-1-one, 3,4,5-trimethyl-	—	0.21%	0.14%
	24.8	1,4-dihydroxy-p-menth-2-ene	0.74%	0.21%	0.79%
	25.9	2,6-Dimethyl-1-nonen-3-yn-5-ol	1.53%	—	0.17%
	28.0	3-Heptyne-2,6-dione, 5-methyl-5-(1-methylethyl)-	—	0.66%	0.39%
	31.1	Ethanone, 1-(1-hydroxy-2,6,6-trimethyl-2,4-cyclohexadien-1-yl)-	0.59%	0.30%	0.35%
	33.2	Benzenemethanol, .alpha.-ethyl-4-methoxy-	—	0.08%	—
	34.4	cis,trans-5,9-Cyclododecadiene-cis-1,2-diol	—	0.21%	0.21%
	35.1	Falcarinol	—	—	0.08%
	46.7	3-buten-2-one, 4-(5,5-dimethyl-1-oxaspiro(2.5)oct-4-yl)	0.43%	0.24%	—
	49.9	2-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]cyclohex-1-en-1-carboxaldehyde	—	0.10%	—
	55.1	1-Decanol, 2-hexyl-	1.23%	—	—
	58.3	1-Heptatriacotanol	0.37%	0.20%	—
	69.3	Methanocyclopenta(a)cyclopropa(e)cyclodecenone, octahydro-trihydroxy-bis(hydroxymethyl)-trimethyl-	0.32%	—	—
Phenol deriv.	19.7	Phenol	0.27%	—	—
	24.1	Phenol, 2-methoxy-	2.31%	0.62%	1.01%
	27.1	Phenol, 4-ethyl	0.81%	—	0.09%
	28.1	2-Methoxy-5-methylphenol	0.56%	—	0.11%
	31.1	Phenol, 4-ethyl-2-methoxy-	1.78%	—	0.02%
	34.1	Phenol, 2-methoxy-4-propyl-	0.77%	—	0.36%
	61.4	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	—	—	0.05%
N-compounds	6.8	1H-Pyrazole, 1,5-dimethyl-	—	—	0.22%
	11.7	Pyrazine, methyl-	1.25%	—	0.52%
	12.0	4-Aminopyridine	0.34%	0.54%	0.02%
	12.9	6-Heptene-1-nitrile	0.39%	—	—
	16.1	Pyrimidine, 4,6-dimethyl-	1.30%	—	0.05%
	16.3	Pyrrolidine, 2-(cyanomethylene)-	1.10%	—	0.05%
	20.1	Phenprobamate	—	—	1.31%
	20.7	1H-Indazole, 4,5,6,7-tetrahydro-	0.25%	—	0.12%
	21.2	1,2,5-Trimethylpyrrole	—	—	0.12%
	25.6	1H-Pyrrole, 3-ethyl-2,4,5-trimethyl-	—	—	0.24%
	26.3	2,5-Pyrrolidinedione, 1,3-diethyl-3-methyl-	0.44%	—	—
	28.6	4-(2,5-Dihydro-3-methoxyphenyl)butylamine	—	—	0.06%
	30.8	4-Isopropenyl-1-methylbicyclo(4.1.0)heptan-2-one oxime	0.36%	—	—
	31.3	2,4-Imidazolidinedione, 1-methyl-	—	—	0.43%
	34.4	N-(2-Hydroxyethyl)succinimide	0.47%	—	—
	34.7	1-(Piperidin-1-yl)hexadecan-1-one	1.08%	—	0.04%
	36.9	Acetamide, N-methyl-N-(4-(3-hydroxypyrrolidinyl)-2-butynyl)-	—	0.24%	—
	37.4	2-Pyrrolidinone, 5-(cyclohexylmethyl)-	1.54%	—	—
	44.3	2-Cyclohexylpiperidine	0.29%	—	—
	46.4	Cyclopropa(d)naphthalen-3-one, octahydro-2,4a,8,8-tetramethyl-, oxime	—	0.02%	—
	50.7	2,3-Diazabicyclo(2.2.1)hept-2-ene, 1,4-diphenyl-	0.62%	—	—

52.2	Pyrrolidine, 1-(4-(4-chlorophenyl)-3-phenyl-2-butenyl)-	0.10%	—	—

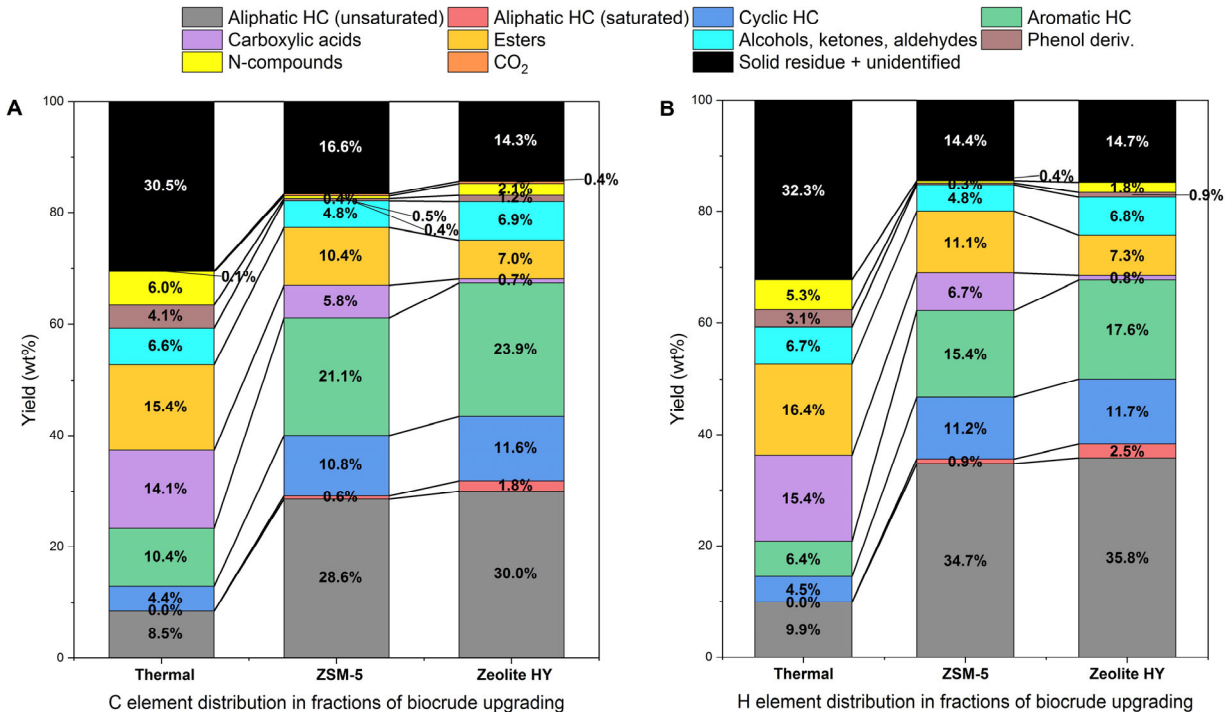

Figure S1. C and H elements distribution in the products of thermal and catalytic cracking of HTL biocrude calculated based on the Py-GC-MS analyses (**A**) C element distribution, (**B**) H element distribution.

$$C_{distr} = \left(Cmpd_{real} \times C_{share\_cmpd} \times (1 - m_{residue}) \times S_{ident}\right) / C_{biocrude}$$

where:

C_{distr} - means the relative share of element C in particular compound detected after thermal/catalytic cracking;

$Cmpd_{real}$ – the relative share of particular compound (Table A3);

C_{share_cmpd} – the share of C element in particular compound;

$m_{residue}$ – mass of residue after test (Table A2);

S_{ident} – share of total peak area of identified compounds on GC-MS chromatogram;

$C_{biocrude}$ – C element content in biocrude subjected to upgrading;

$$H_{distr} = \left(Cmpd_{real} \times H_{share\_cmpd} \times (1 - m_{residue}) \times S_{ident}\right) / H_{biocrude}$$

where:

H_{distr} - means the relative share of element H in particular compound detected after thermal/catalytic cracking;

$Cmpd_{real}$ – the relative share of particular compound (Table A3);

H_{share_cmpd} – the share of H element in particular compound;

$m_{residue}$ – mass of residue after test (Table A2);

S_{ident} – share of total peak area of identified compounds on GC-MS chromatogram;

$H_{biocrude}$ – H element content in biocrude subjected to upgrading.