ELECTRONIC SUPPLEMENTARY INFORMATION

Laboratory scale conceptual process development for the isolation of renewable glycolaldehyde from pyrolysis oil to produce fermentation feedstock

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1. Detail experimental procedure

1.1. Materials

The raw material was forest residue-derived pyrolysis oil obtained from VTT Finland. It was produced by fast pyrolysis at 520 °C and a residence time of 1 s. At the time of experiments, it contained 6.4 wt% glycolaldehyde, 5.2 wt% acetic acid, 1.4 wt% acetol, 0.2 wt% furfural, and 0.4 wt% furanone. TOA (≥98%), 1-octanol (≥99.5%), toluene (99.8%), nonane (≥95%), and dibenzofuran (≥99%) were purchased from Sigma-Aldrich. Ethanol (≥99.5%) was received from Merck Chemicals. MiliQ water was used as solvent. All chemicals were used without further purification.

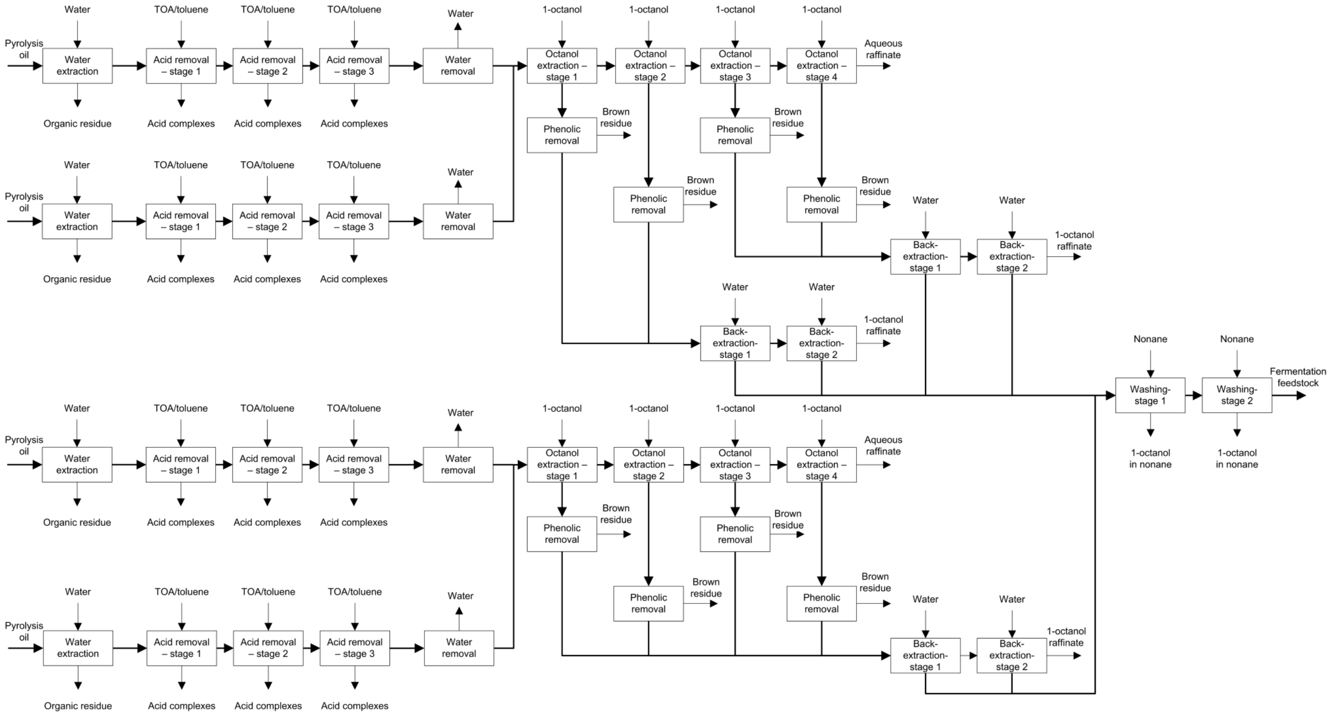

Fig. S1 Actual laboratory batch experiment scheme for process development

1.2. Methods

The batch experiments were conducted using the scheme illustrated in Fig. S1. Water and phenolic removal steps were distillation while the others were extraction.

All extraction experiments were performed at 20 °C and 1 bar in 1 L-erlenmeyer flasks equipped with magnetic stirring bars. After extraction, the mixture was allowed to settle for at least 2 h to ensure complete phase separation. Multistage extraction was done cross-currently by adding fresh solvent to each stage. Distillation experiments were carried out in a batch

SPALTROHR® distillation column from Fischer with 90 theoretical stages.

1.3. Analysis

For GC analysis, 350 µL sample was mixed with 125 µL internal standard solution of 0.025 M dibenzofuran in ethanol and then diluted with 1300 µL ethanol. The quantitative analyses were performed in Varian CP 3900 equipped with an FID detector and a capillary column CP-Wax 52CB (30 m × 0.53 mm; 1 µm). Helium was used as carrier gas at a constant velocity of 2 mL/min. Split ratio was 50. The injector temperature was 250 °C, while that of detector was 280 °C. The initial oven temperature was 45 °C and then ramped at 10 °C/min to 60 °C, 3 °C/min to 160 °C, and 10 °C/min to 250 °C, which was maintained for 56 minutes. The accuracy of the analytical method was determined to be within 5%.

1.4. Definitions

Distribution coefficient and yield are used to denote extraction performance. The distribution coefficient of component *i* (D_i) is calculated as the ratio of the mass fraction of component *i* in the extract phase ($x_{i,extract}$) to that in the raffinate phase ($x_{i,raffinate}$) at equilibrium.

$$D_i = \frac{x_{i,extract}}{x_{i,raffinate}}$$

The extraction yield of component *i* (Y_i) is the mass of component *i* in the extract phase ($m_{i,extract}$) divided by its initial mass in the extraction feed ($m_{i,feed}$) at equilibrium.

$$Y_i = \frac{m_{i,extract}}{m_{i,feed}}$$

2. Extraction performance

Table S1 Extraction performance of water extraction

Compound	Distribution coefficient, D (-)	Yield, Y (%)
Glycolaldehyde	0.63	63.1
Acetic acid	2.67	87.9
Acetol	7.45	95.3
Furfural	1.06	74.2
Furanone	0.18	32.5

Table S2 Extraction performance of the acid removal step

Compound	Stage 1		Stage 2		Stage 3	
	D (-)	Y (%)	D (-)	Y (%)	D (-)	Y (%)
Glycolaldehyde	0.02	0.0	0.01	0.2	0.04	1.3
Acetic acid	2.34	65.0	0.95	28.7	1.02	25.6
Acetol	0.00	0.0	0.00	0.0	0.05	1.8
Furfural	6.80	85.3	0.00	0.0	0.10	3.4
Furanone	0.00	0.0	0.04	1.7	0.49	16.9

Table S3 Performance of octanol extraction

Compound	Stage 1		Stage 2		Stage 3		Stage 4	
	D (-)	Y (%)	D (-)	Y (%)	D (-)	Y (%)	D (-)	Y (%)
Glycolaldehyde	0.25	9.3	0.22	9.4	0.27	10.4	0.29	8.5
Acetic acid	0.51	14.6	0.56	19.6	0.46	19.0	0.44	13.0
Acetol	0.17	5.9	0.14	6.1	0.15	6.1	0.06	2.2
Furfural	1.44	44.7	1.44	45.3	1.90	50.9	2.89	61.6
Furanone	0.24	8.8	0.20	8.3	0.20	8.5	0.21	5.9

Table S4 Distribution coefficients and yields of the back-extraction

Compound	Stage 1		Stage 2		Stage 3	
	D (-)	Y (%)	D (-)	Y (%)	D (-)	Y (%)
Glycolaldehyde	4.49	54.1	4.04	53.7	3.79	31.5
Acetic acid	1.18	24.9	1.07	20.5	0.97	10.1
Acetol	10.25	95.3	11.46	75.6	8.88	55.7
Furfural[a]	n/d	n/d	n/d	n/d	n/d	n/d
Furanone	3.50	51.8	4.14	52.7	3.35	28.2

[a] Furfural was not quantified since its concentration was below the detection limit