Supporting Information

Integrating Catalytic Fractionation and Microbial Funneling to produce 2-Pyrone-4,6-Dicarboxylic Acid and Ethanol

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Table of Supplemental Data

Biological Conversion

Microbial funneling of RCF-oil to PDC

Growth curves for microbial funneling of RCF-products by the PDC producing strain of *N. aromaticivorans*.

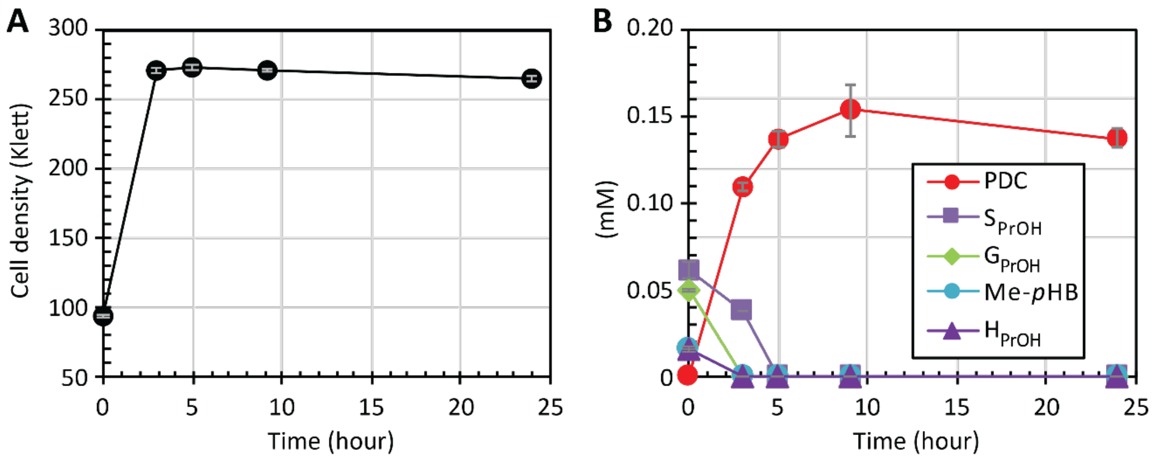

Fig. S1. (A) Cell density and (B) extracellular metabolite concentration of cultures supplemented with hydrogenolysis mixture obtained by catalytic hydrogenolysis of poplar.

Table S1. HPLC-MS experimental results for RCF-oil to PDC conversion.

Experiment	PDC (mM)	mmol PDC / L RCF-oil in solvent	g PDC / L RCF-oil in solvent	g PDC / Kg Poplar	Yield (% w/w)
Run 1	0.138	13.8	2.5	55.2	5.5%
Run 2	0.16	15.8	2.9	63.4	6.3%
Run 3	0.14	14.2	2.6	56.8	5.7%
Average	0.15±0.01	14.6±0.9	2.68±0.16	58.5±3.5	5.8%±0.4%

Microbial funneling RCF-pulp hydrolysate to ethanol

Growth curves for *S. cerevisiae* GLBRCY945[23] growing on hydrolysate produced from RCF-pulp.

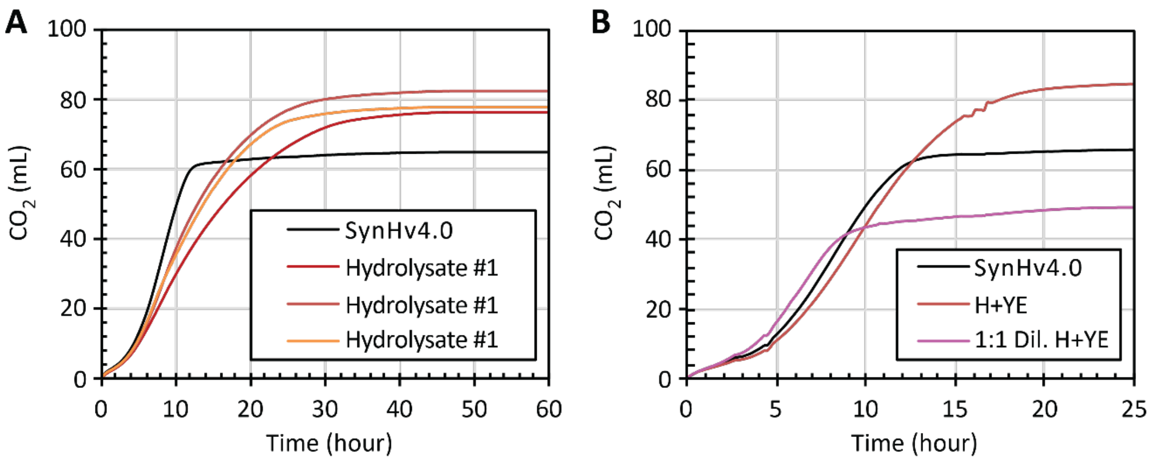

Fig. S2. Respirometer fermentation of yeast Y945 in Pd/C-pretreated poplar hydrolysate (A) without yeast extract, (B) Pd/C-pretreated poplar hydrolysate with yeast extract 10 g/L yeast extract (H+YE) and with the hydrolysate diluted 1:1 (v/v) with water and 5 g/L yeast extract (1:1 Dil. H+YE).

Table S2. HPLC-RID experimental results for RCF-pulp hydrolysate sugar composition and product composition after fermentation.

Compound	RCF-pulp hydrolysate	Synthetic hydrolysate v4.0	RCF-pulp spent liquor #1	RCF-pulp spent liquor #3	RCF-pulp spent liquor #3
Ethanol (g/L)	N/D	40.4	61.7	63.4	62.0
Glucose (g/L)	100.38	N/D	N/D	N/D	N/D
Xylose (g/L)	42.46	19.9	15.3	18.2	13.2
Cellobiose (g/L)	6.27	N/D	3.2	4.0	2.8
Glycerol (g/L)	0.2	3.3	4.2	3.9	4.2
Acetate (g/L)	N/D	3.9	0.3	0.2	0.3

N/D = Not detected

Process Synthesis

ASPEN PLUS mode

Fig. S3 shows the process configuration of the RCF and MNP blocks simulated in ASPEN PLUS. The processing capacity of the biorefinery is 2000 metric tons of dry biomass per day, consistent with NREL designs. Biomass, hydrogen, and methanol are fed into RCF reactor (RCFR). After hydrogenolysis of the biomass in the reactors, a series of flash tanks (FLH1,2,3) are used to separate most of the excess methanol and hydrogen, and water from the biomass from the mixture. The remaining mixture is sent to a centrifuge (CNF) where the carbohydrate pulp is separated and sent for hydrolysis. The liquid stream consisting primarily of monomer, oligomer, and methanol, is sent for distillation (DST1), where the distillate stream containing monomer is cooled (CLR1) and sent for PDC production. The vapor streams from the flash tanks are sent to are sent to another two-stage flash tanks where the first is used to separate hydrogen (FLH4) while the second is used to reduce the methanol content further (FLH5) before the remaining stream is distilled (DST2) to separate the remaining methanol and water. The bottoms stream containing the wastewater is sent for treatment. The distillate stream consisting of methanol is combined with fresh methanol, and other methanol streams. The pressure of the methanol stream pressure is increased using a pump and preheated using the vapor streams from the flash tanks by heat exchangers (HX1,2,3) and finally heated to meet RCF reactor conditions. The hydrogen stream is compressed (CPR) using a multi-stage compressor equipped with electric heaters to meet reactor conditions.

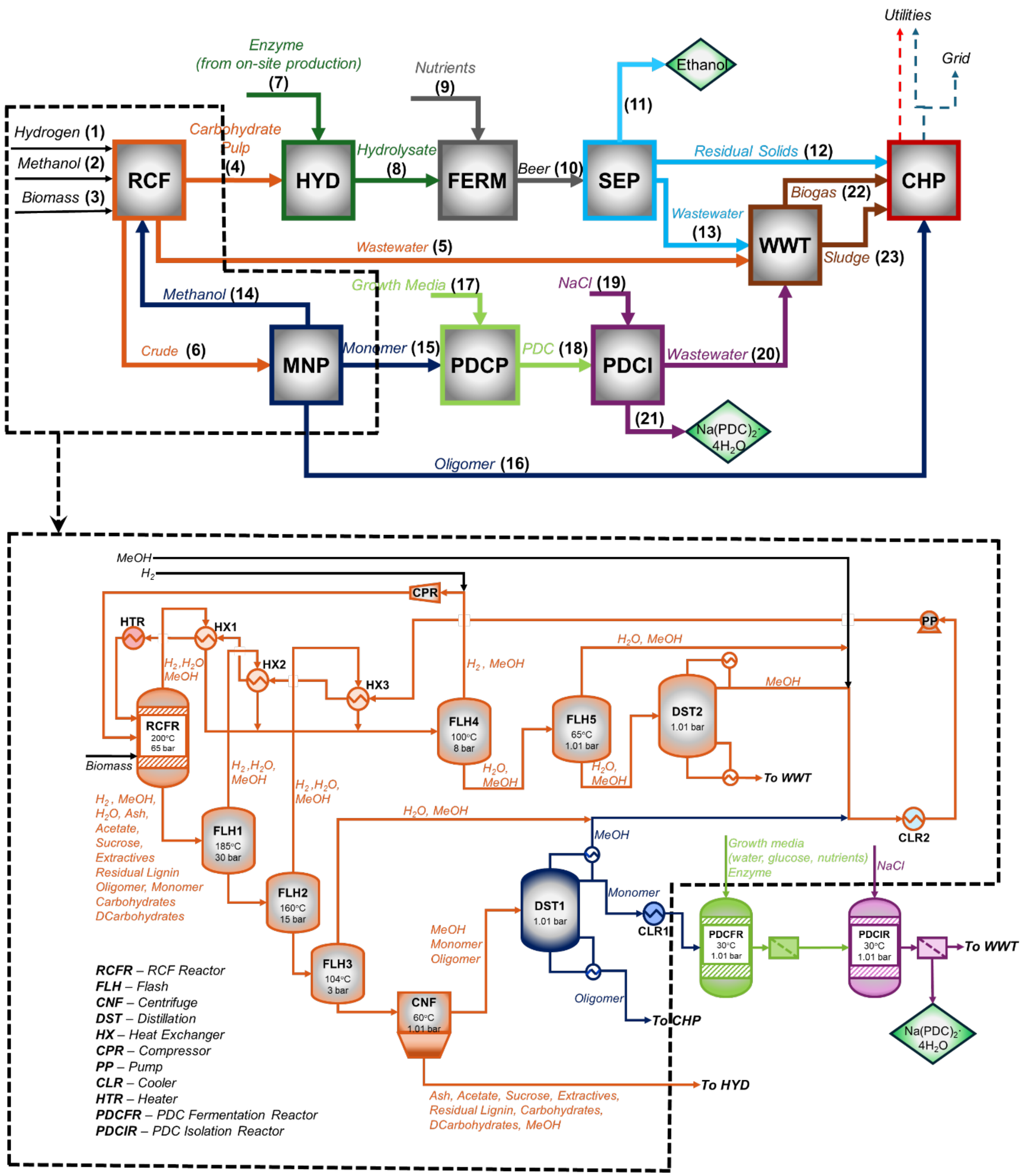

Fig. S3. Process description of RCF and MNP blocks developed and simulated in ASPEN PLUS

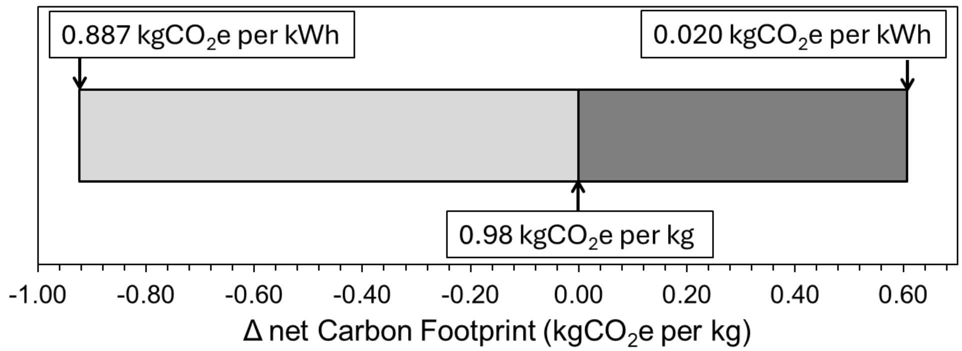

Fig. S4. Sensitivity analysis showing impact of grid emission factor on net carbon footprint

Economic parameters and assumptions

Table S3 indicates the biomass (poplar) feedstock composition on dry basis, and the corresponding moisture content. Table S4 gives the detailed capital and operating cost for the base case biorefinery. Table S5 gives the economic parameters, and the economic assumptions used for the analysis, while Table S6 gives the emissions factors.

Table S3. Feedstock composition

Component	Weight % (dry basis)
Glucan	46.6%
Xylan	16.2%
Arabinan	0.6%
Mannan	2.9%
Galactan	0.8%
Sucrose	0.5%
Acetate	4.3%
Extractives	3.6%
Lignin	24.2%
Ash	0.3%
Total	100%
Moisture	17%

Table S4. Summary of capital and operating expenditure for base case (all values in 2024$)

Capital Costs	
Reductive Catalytic Fractionation (RCF)	$463,127,397
Hydrolysis (HYD, Including Enzyme Production)	$21,583,784
Fermentation (FERM)	$12,808,794
Ethanol Separation & Storage (SEP)	$12,595,635
Wastewater Treatment (WWT)	$66,685,271
Combined Heat and Power Generation (CHP)	$110,185,780
Monomer Purification (MNP)	$7,579,711
PDC Production (PDCP)	$33,406,892
PDC Isolation (PDCI)	$8,169,016
Total Installed Equipment Cost	$736,142,281
Added Direct + Indirect Costs	$718,850,582
(% of TCI)	49%
Total Capital Investment (TCI)	$1,454,992,863
Capital Recovery Charge	0.347
Manufacturing Costs ($/yr)	
Feedstock	$75,516,342
Make-up Solvent + Hydrogen	$24,021,422
Catalyst	$931,978
PDC Production Growth Media	$54,355,250
Glucose (Enzyme Production)	$19,814,681
Other Chemicals	$4,838,629
Net Electricity	-$5,530,443
Ethanol	-$59,883,443
Fixed Costs	$94,049,538
Capital Depreciation	$46,131,580
Average Income Tax	$90,720,454
Average Return on Investment	$368,195,498

Table S5. List of economic parameters, and assumptions

Biomass ($ per ton dry biomass)[a]	114.95
Methanol ($ per ton)[i]	463.1
Hydrogen ($ per ton)[e]	1479.6
Glucose ($ per ton)[e]	1109.6
Electricity ($ per kWh)[d]	0.0808
Natural Gas ($ per ton)[e]	312.7
Cooling Water ($ per ton)[j]	0.000299
Disposal of ash ($ per ton)[g]	48.3
Boiler chemicals ($ per ton)[g]	7582.6
FGD lime ($ per ton)[g]	302.7
Fresh Water ($ per ton)[e]	0.65
Disodium phosphate ($ per ton)[e]	497.5
Monopotassium phosphate ($ per ton)[b]	1113.0
Ammonium Sulfate ($ per ton)[h]	347.6
NaCl ($ per ton)[k]	124.9
Corn steep liquor ($ per ton)[f]	103.4
Caustic ($ per ton)[g]	2108
Investment Tax Credit[l]	30%
Renewable Identification Number under Renewable Fuels Standard Program ($ per gal EGE)[m]	3.5
Clean Fuels Production Credit ($ per gal EGE)[n]	1
Ethanol selling price ($ per GGE)[a]	2.50

- All costs are indexed to 2024 dollars. Economic assumptions consistent with NREL reports[16,24,25]
- Internal rate of return (IRR) is assumed to be 30% to reflect the higher risk in investing in new technology[5]
- Capital investment is spread over three years at a rate of 8%, 60%, and 32% in the first, second, and third years, respectively
- Working capital is 5% of fixed capital investment
- Total direct cost (TDC) is 117.5% of installed cost (IC)
- Total indirect cost (TIC) is 60% of TDC
- Working capital is 5% of fixed capital investment (FCI = TCD + TIC)
- Maintenance cost is 3% of IC
- Total salaries and labor burden is 4.5% of FCI
- Property insurance and tax is 0.7% of FCI
- Equity financing is 40%
- Loan term is 10 years with 8% interest rate
- Federal income tax rate is 35%
- State taxes are not considered primarily because tax rates vary from state to state (0% to 12%)
- Start-up time is 6 months
- Revenues, variable costs, and fixed costs during start-up (% of normal) are 50%, 75%, and 100% respectively
- Depreciation for general and steam plants is 200% and 150% declining balance
- General and steam plant recovery periods are 7 and 20 years respectively

[a]Taken from Bartling *et al.*,[10] [b]Taken from Alibaba,[26] [d]Taken from EIA,[27] [e]Taken from NREL 2018,[24] [f]Taken from NREL 2011,[16] [g]Taken from NREL 2015,[25] [h]Taken from Intratec,[28] [i]Taken from Liao *et al.*,[29] [j]Estimated from Aspen Process Economic Analyzer, [k]Taken from Indywaterpros,[30] [l]Taken from Crux,[17] [m]Taken from EPA,[18] [n]Taken from DOE[19]

Table S6. Emission Factors of carbon footprint analysis

Biomass (poplar) soil organic carbon (SOC) (kg CO_2e per kg)[a]	-0.1250
Biomass (poplar) farming (CH_4+N_2O emissions) and transportation (kg CO_2e per kg)[b]	0.0748
Catalyst (5 wt% Pd/C) (kg CO_2e per kg)[b]	12.044
Hydrogen (kg CO_2e per kg)[b]	9.3227
Methanol (kg CO_2e per kg)[b]	0.4640
Ash disposal (landfill) (kg CO_2e per kg)[b]	0.0589
FGD lime (kg CO_2e per kg)[b]	0.0385
Fresh water (kg CO_2e per kg)[b]	0.0063
Glucose (kg CO_2e per kg)[b]	0.7482
Disodium phosphate (kg CO_2e per kg)[b]	1.4503
Monopotassium phosphate (kg CO_2e per kg)[b]	1.9002
Ammonium Sulfate (kg CO_2e per kg)[b]	0.4831
NaCl (kg CO_2e per kg)[b]	0.2587
Corn steep liquor (kg CO_2e per kg)[b]	1.6095
Caustic (NaOH) (kg CO_2e per kg)[b]	1.9661
Electricity (average US electricity grid, kg CO_2e per kWh)[b]	0.3637
Cellulase enzyme (kg CO_2e per kg)[b]	2.0816
Electricity (coal power plant, kg CO_2e per kWh)[b]	1.0492
Electricity (natural gas power plant, kg CO_2e per kWh)[b]	0.4507
Electricity (residual oil power plant, kg CO_2e per kWh)[b]	0.9594
Gasoline (kg CO_2e per kg)[b]	0.7028
Natural Gas as fuel (kg CO_2e per kg)[b]	0.3238

[a]Taken from Gelfand et al.,[32] [b]Taken from Wang et al.[31]

Note: The reported emissions in Argonne GREET[40] (g species [CO_2, N_2O, CH_4] per shot ton) were converted to kgCO_2e per kg by applying a 100-year global warming potential (CO_2 = 1; N_2O = 273; CH_4 = 30) and then using the conversion factor: kgCO_2e per kg = 1.10231×10^{-6} gCO_2e per shot ton.