Electronic Supplementary Information

Solvent Selection for a Biomass-to-Bioproduct Pipeline through Integrated Reductive Catalytic Fractionation and Microbial Funneling

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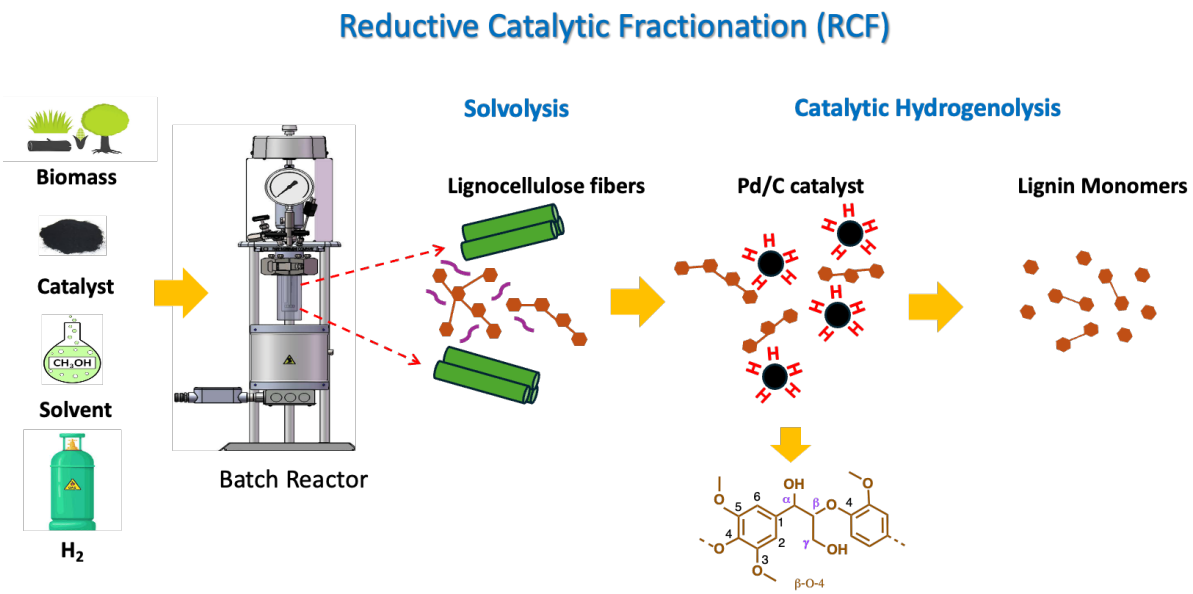

Fig. S1 Scheme depicting the RCF methodology involving solvolysis and catalytic hydrogenolysis.

Table S1. Boiling point (ºC) and vapor pressure (bar) data for solvents methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA), 1,4-dioxane (Diox) and ethylene glycol (EG).

Solvent	**MeOH**	**EtOH**	**IPA**	**IBA**	**Diox**	**EG**
Boiling Point (ºC)	64.7	78.5	82.4	108	101.2	197.3
Vapor Pressure at 200 ºC (bar)	40*	30*	26*	25*	4.9*	1*

*Estimated from COSMO-RS[1]

Table S2. RCF reaction pressure (bar), and monomer and PDC yields (wt% biomass and wt% lignin) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox). Reaction conditions: T = 200 °C, initial pressure = 30 bar (except EG: 5 bar, EG/water mixtures: 15 bar, and Diox: 20 bar), t = 2 h, 30 mL solvent, biomass/catalyst = 18.

Solvent system	Reaction Pressure (bar)	RCF Yield (wt% biomass)	RCF Yield (wt% lignin)	PDC Yield (wt% biomass)	PDC Yield (wt% lignin)
Ethylene Glycol (EG)	7	5.1 ± 0.1	21.4 ± 0.3	3.5 ± 0.3	14.8 ± 1.3
EG/water - 5 vol%	21	5.7 ± 0.4	23.8 ± 1.7	3.7 ± 0.1	15.5 ± 0.3
EG/water - 15 vol%	21	5.6 ± 0.2	23.5 ± 0.7	4.5 ± 0.0	18.5 ± 0.1
EG/water - 25 vol%	21	6.0 ± 0.1	24.9 ± 0.4	4.8 ± 0.1	20.1 ± 0.5
EG/water - 50 vol%	21	6.6 ± 0.2	27.6 ± 0.8	5.6 ± 0.2	23.5 ± 0.6
Methanol (MeOH)	60	4.9 ± 0.2	20.6 ± 0.8	4.6 ± 0.0	19.0 ± 0.0
MeOH/water - 5 vol%	56	4.6 ± 0.6	19.3 ± 2.6	4.4 ± 0.9	18.4 ± 3.7
MeOH/water - 15 vol%	54	5.6 ± 0.1	23.5 ± 0.4	5.3 ± 0.2	22.0 ± 0.9
MeOH/water - 25 vol%	52	6.9 ± 0.2	28.7 ± 1.0	6.0 ± 0.4	24.8 ± 1.8
MeOH/water - 50 vol%	48	8.5 ± 0.5	35.5 ± 2.0	6.3 ± 0.6	26.4 ± 2.7
Ethanol (EtOH)	54	4.9 ± 0.3	20.3 ± 1.2	2.8 ± 0.1	11.8 ± 0.4
EtOH/water - 5 vol%	54	4.0 ± 0.0	16.7 ± 0.0	3.7 ± 0.1	15.5 ± 0.3
EtOH/water - 15 vol%	52	4.9 ± 0.1	20.4 ± 0.5	4.5 ± 0.0	18.5 ± 0.1
EtOH/water - 75 vol%	49	5.4 ± 0.0	22.5 ± 0.1	4.8 ± 0.1	20.1 ± 0.5
EtOH/water - 50 vol%	47	8.0 ± 0.4	33.4 ± 1.8	4.9 ± 0.1	20.6 ± 0.4
Isopropanol (IPA)	59	2.7 ± 0.0	11.3 ± 0.1	2.4 ± 0.5	10.2 ± 1.9
IPA/water - 5 vol%	56	3.7 ± 0.2	15.3 ± 0.7	3.7 ± 0.1	15.4 ± 0.3
IPA/water - 15 vol%	54	4.4 ± 0.0	18.4 ± 0.1	4.4 ± 0.0	18.5 ± 0.1
IPA/water - 25 vol%	49	6.1 ± 0.1	25.4 ± 0.4	4.8 ± 0.1	20.1 ± 0.5
IPA/water - 50 vol%	46	9.3 ± 0.3	38.8 ± 1.1	6.4 ± 0.1	26.6 ± 0.2
Isobutanol (IBA)	46	2.8 ± 0.1	11.5 ± 0.6	1.4 ± 0.1	5.7 ± 0.4
IBA/water - 5 vol%	46	3.3 ± 0.2	13.8 ± 0.8	0.7 ± 0.4	3.0 ±1.6
IBA/water - 15 vol%	46	4.6 ± 0.3	19.3 ± 1.3	1.4 ± 0.2	5.8 ± 0.8
IBA/water - 25 vol%	46	5.2 ± 0.2	21.5 ± 0.7	1.7 ± 0.3	7.1 ± 1.2
IBA/water - 50 vol%	44	9.4 ± 0.2	39.2 ± 0.7	2.3 ± 0.1	9.7 ± 0.4
1,4-dioxane (Diox)	30	1.6 ± 0.3	6.7 ± 1.1	1.9 ± 0.1	7.9 ± 0.5
Diox/water - 5 vol%	33	2.2 ± 0.4	9.2 ± 1.6	2.6 ± 0.2	11.0 ± 0.8
Diox/water - 15 vol%	34	2.7 ± 0.4	11.1 ± 1.8	3.1 ± 0.6	13.0 ± 2.5
Diox/water - 25 vol%	32	3.3 ± 0.6	13.9 ± 2.7	4.0 ± 0.3	16.8 ± 1.2
Diox/water - 50 vol%	30	5.5 ± 0.6	23.1 ± 2.4	5.9 ± 0.8	24.7 ± 3.4

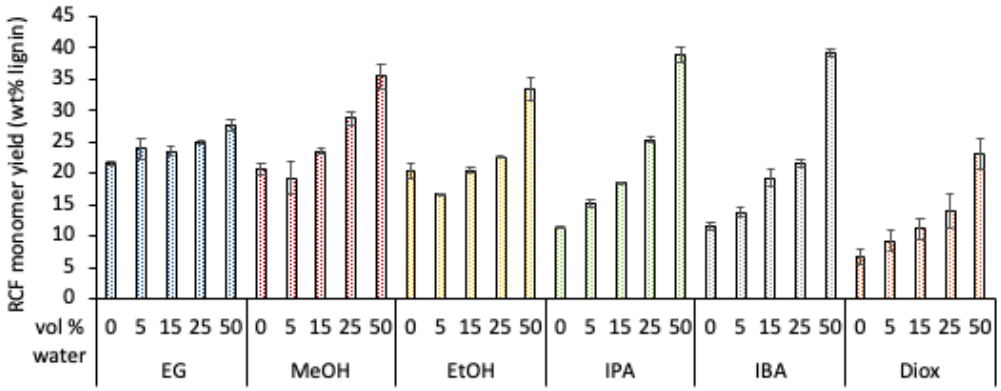

Fig. S2. RCF monomer yield (wt% lignin) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox). Reaction conditions: T = 200 °C, initial pressure = 30 bar (except EG: 5 bar, EG/water mixtures: 15 bar, and Diox: 20 bar), t = 2 h, 30 mL solvent, biomass/catalyst = 18

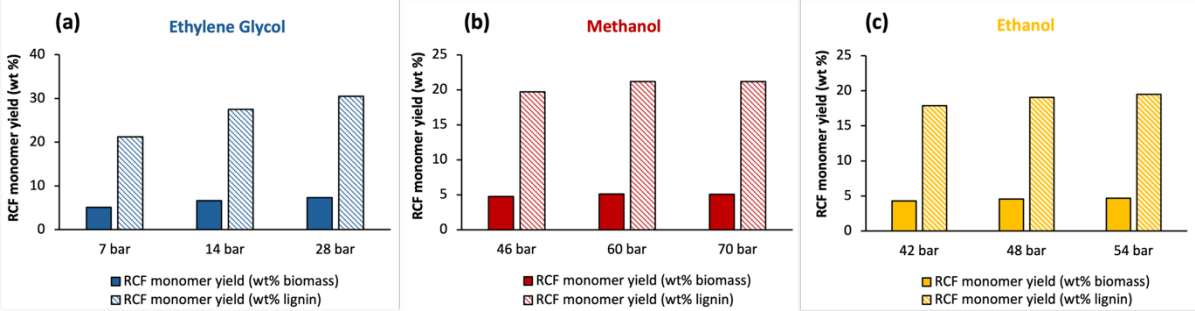

Fig. S3. Effect of reaction pressure on RCF monomer yield (wt%) on a biomass and lignin basis with pure solvents of methanol (MeOH), ethanol (EtOH), and ethylene glycol (EG). Reaction conditions: T = 200 °C, initial pressure = MeOH: 22-39 bar, EtOH: 20-30 bar, EG: 5-20 bar, t = 2 h, 30 mL solvent, biomass/catalyst = 18.

Table S3a. RCF Monomer distribution (wt%) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox). Reaction conditions: T = 200 °C, initial pressure = 30 bar (except EG: 5 bar, EG/Water mixtures: 15 bar, Diox: 20 bar), t = 2 h, 30 mL solvent, biomass/catalyst = 18.

Solvent & Solvent/Water Mixture		**Propanol**	**Propane**	**Esters**	**Methyl**	**Ethyl**	**Phenol**
Solvent	**Water vol%**	wt%	wt%	wt%	wt%	wt%	wt%
Ethylene Glycol (EG)	0	88.3 ± 0.0	10.8 ± 0.0	0.0 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
	5	81.1 ± 0.8	12.4 ± 1.5	5.8 ± 0.8	0.2 ± 0.0	0.3 ± 0.1	0.3 ± 0.0
	15	75.2 ± 1.4	15.8 ± 1.5	7.8 ± 0.5	0.3 ± 0.1	0.6 ± 0.2	0.3 ± 0.0
	25	70.8 ± 1.3	17.8 ± 1.5	9.8 ± 0.5	0.3 ± 0.1	0.9 ± 0.2	0.3 ± 0.1
	50	61.9 ± 3.9	24.9 ± 3.8	10.2 ± 1.4	0.4 ± 0.1	2.1 ± 1.4	0.4 ± 0.0
Methanol (MeOH)	0	77.5 ± 0.9	9.2 ± 0.3	12.5 ± 1.3	0.3 ± 0.0	0.2 ± 0.0	0.3 ± 0.0
	5	75.9 ± 3.3	10.6 ± 1.3	12.6 ± 2.0	0.3 ± 0.0	0.4 ± 0.1	0.3 ± 0.0
	15	76.2 ± 0.9	10.3 ± 0.3	12.3 ± 0.4	0.3 ± 0.0	0.7 ± 0.2	0.3 ± 0.0
	25	75.7 ± 0.5	10.7 ± 0.9	12.2 ± 0.4	0.3 ± 0.1	0.8 ± 0.0	0.3 ± 0.0
	50	73.4 ± 0.8	13.5 ± 0.1	11.0 ± 0.7	0.4 ± 0.0	1.4 ± 0.0	0.3 ± 0.0
Ethanol (EtOH)	0	75.4 ± 2.1	9.6 ± 0.8	14.2 ± 1.2	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
	5	74.6 ± 0.0	10.0 ± 0.1	14.6 ± 0.2	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
	15	73.2 ± 0.6	10.3 ± 0.1	15.2 ± 0.5	0.4 ± 0.0	0.6 ± 0.1	0.3 ± 0.0
	25	72.2 ± 0.1	11.3 ± 0.2	15.0 ± 0.4	0.4 ± 0.0	0.9 ± 0.1	0.3 ± 0.0
	50	70.6 ± 0.7	13.8 ± 0.1	13.2 ± 0.8	0.5 ± 0.1	1.5 ± 0.0	0.3 ± 0.0
Isopropanol (IPA)	0	69.2 ± 4.5	9.9 ± 0.5	19.9 ± 3.9	0.3 ± 0.0	0.5 ± 0.1	0.2 ± 0.0
	5	70.4 ± 0.6	10.0 ± 0.1	18.6 ± 0.9	0.3 ± 0.0	0.5 ± 0.1	0.3 ± 0.0
	15	69.4 ± 0.1	10.5 ± 0.1	18.6 ± 0.2	0.4 ± 0.1	0.7 ± 0.0	0.3 ± 0.0
	25	70.8 ± 0.9	11.3 ± 0.2	16.2 ± 0.6	0.5 ± 0.0	1.0 ± 0.1	0.3 ± 0.0
	50	71.5 ± 0.2	12.9 ± 0.0	13.4 ± 0.3	0.5 ± 0.1	1.6 ± 0.0	0.2 ± 0.0

Table S3b. Continuation of RCF Monomer distribution (wt%) with pure solvents and aqueous mixtures (5-50 vol% water) of isobutanol (IBA) and 1,4-dioxane (Diox).

Solvent & Solvent/Water Mixture		**Propanol**	**Propane**	**Esters**	**Methyl**	**Ethyl**	**Phenol**
Solvent	**Water vol%**	wt%	wt%	wt%	wt%	wt%	wt%
Isobutanol (IBA)	0	71.4 ± 1.2	9.4 ± 0.7	18.2 ± 2.0	0.3 ± 0.0	0.4 ± 0.1	0.2 ± 0.0
	5	76.9 ± 0.1	11.1 ± 0.5	11.0 ± 1.0	0.3 ± 0.0	0.5 ± 0.4	0.2 ± 0.0
	15	77.1 ± 0.5	11.9 ± 0.2	9.7 ± 0.3	0.3 ± 0.0	0.7 ± 0.0	0.2 ± 0.0
	25	75.9 ± 0.7	12.6 ± 0.3	10.0 ± 0.3	0.4 ± 0.0	1.0 ± 0.0	0.1 ± 0.0
	50	77.6 ± 0.1	14.8 ± 0.5	6.6 ± 0.4	0.3 ± 0.0	0.7 ± 0.0	0.1 ± 0.0
1,4-dioxane (Diox)	0	77.7 ± 2.7	17.7 ± 0.6	3.2 ± 4.6	0.0 ± 0.0	1.2 ± 0.7	0.3 ± 0.4
	5	79.0 ± 3.7	16.9 ± 1.5	3.1 ± 4.4	0.0 ± 0.0	0.7 ± 0.6	0.2 ± 0.3
	15	79.3 ± 2.7	17.7 ± 0.3	2.2 ± 3.1	0.2 ± 0.1	0.2 ± 0.0	0.4 ± 0.0
	25	79.1 ± 2.4	17.8 ± 0.0	1.9 ± 2.7	0.3 ± 0.1	0.7 ± 0.7	0.2 ± 0.3
	50	75.9 ± 1.9	19.4 ± 0.9	3.6 ± 0.8	0.7 ± 0.2	0.3 ± 0.0	0.2 ± 0.1

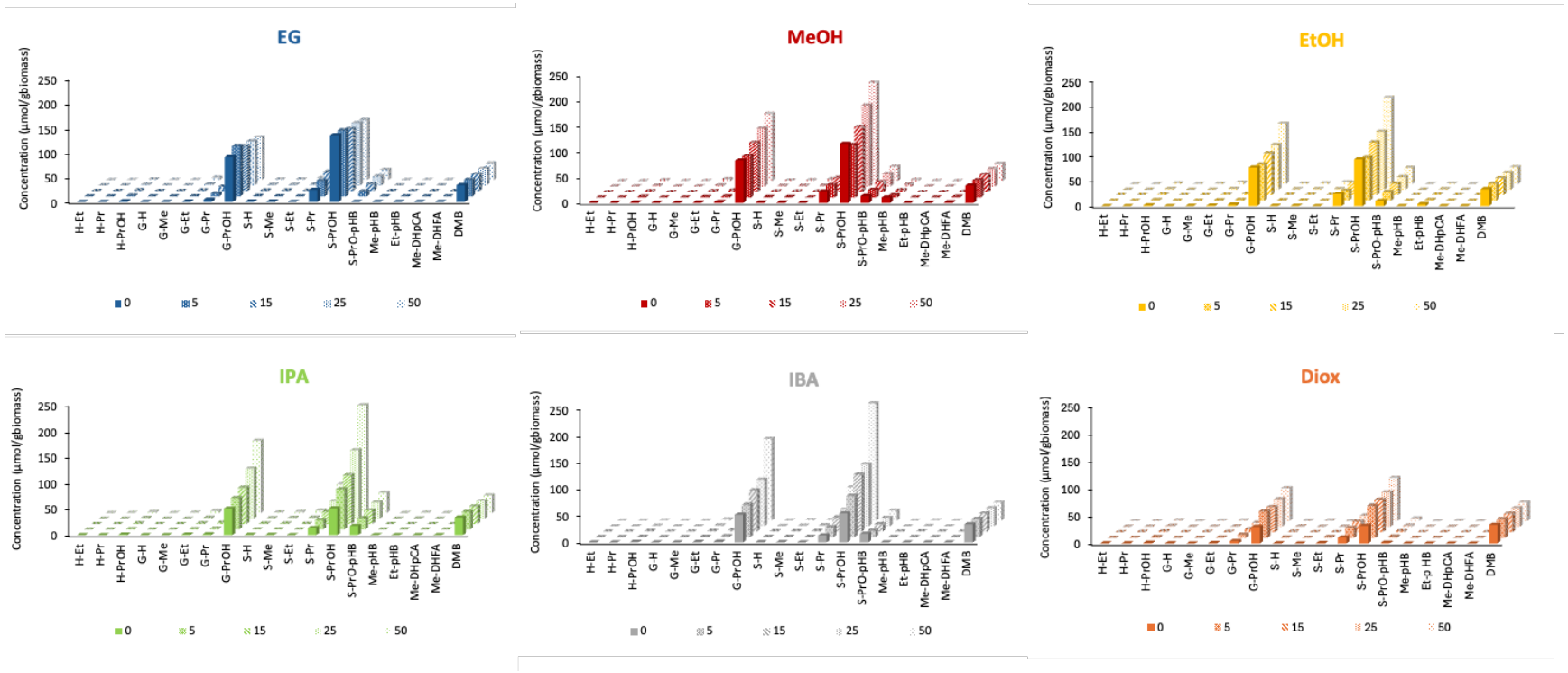

Figure S4. RCF Monomer concentration (µmol/g biomass) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox). Reaction conditions: T = 200 °C, initial pressure = 30 bar (except EG: 5 bar, EG/water: 15 bar, and Diox: 20 bar), t = 2 h, 30 mL solvent, biomass/catalyst = 18.

Table S4a. RCF monomer concentration (µmol/g biomass) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox). Reaction conditions: T= 200 °C, initial pressure = 30 bar (except EG: 5 bar, EG/water mixtures: 15 bar, and Diox: 20 bar), t = 2 h, 30 mL solvent, biomass/catalyst = 18.

Solvent & Solvent Water Mixture		**H-Et**	**H-Pr**	**H-PrOH**	**G-H**	**G-Me**	**G-Et**	**G-Pr**	**G-PrOH**	**S-H**	**S-Me**	**S-Et**	**S-Pr**	**S-PrOH**	**S-PrO-*p*HB**	**Me-*p*HB**	**Et-*p*HB**	**Me-DH*p*CA**	**Me-DHFA**	**DMB**
Solvent	**Water (vol%)**																			
EG	**0**	0.0	0.0	1.4	0.1	0.0	0.8	4.7	90.6	1.0	0.8	0.0	24.3	135.4	0.0	0.0	0.1	0.0	0.0	33.9
	5	0.0	0.1	1.7	0.1	0.0	0.8	6.0	102.4	0.9	0.8	0.1	31.6	133.9	10.2	0.0	0.2	0.0	0.0	33.9
	15	0.0	0.1	1.5	0.2	0.1	1.3	8.7	90.8	1.0	0.9	0.6	38.9	125.7	13.5	0.0	0.2	0.0	0.0	33.9
	25	0.0	0.1	1.4	0.1	0.1	2.0	11.6	89.6	1.1	1.1	1.5	45.9	126.8	18.1	0.0	0.1	0.0	0.0	33.9
	50	0.0	0.2	1.4	0.5	0.3	4.6	19.7	87.0	1.3	1.4	4.0	68.8	121.8	20.7	0.0	0.3	0.0	0.0	33.9
MeOH	0	0.0	0.0	0.8	0.1	0.0	0.8	1.7	82.8	1.0	0.8	0.0	22.6	115.3	13.6	10.6	0.0	0.0	1.3	33.9
	5	0.0	0.0	1.4	0.0	0.0	1.0	2.0	80.4	0.8	0.8	0.1	24.1	102.6	15.1	4.6	0.0	0.0	1.3	33.9
	15	0.1	0.1	1.7	0.1	0.1	1.5	3.1	96.0	1.1	1.0	0.9	28.0	126.9	19.4	3.9	0.2	0.0	0.6	33.9
	25	0.0	0.1	1.8	0.3	0.1	2.0	2.4	113.0	1.2	1.3	1.5	36.9	157.8	24.6	3.5	0.2	0.0	0.0	33.9
	50	0.0	0.1	1.8	0.4	0.5	3.6	10.2	130.8	1.2	1.8	3.7	52.1	191.3	27.8	2.5	0.4	0.0	0.0	33.9
EtOH	0	0.0	0.0	1.4	0.0	0.3	1.2	2.9	77.0	0.6	0.5	0.0	24.0	93.6	10.2	0.0	4.0	0.0	0.0	33.9
	5	0.0	0.0	1.3	0.0	0.0	0.8	1.8	72.7	0.8	0.8	0.0	20.0	85.3	17.7	0.0	1.8	0.0	0.0	33.9
	15	0.1	0.1	1.7	0.1	0.2	1.3	2.6	84.0	1.0	1.1	0.7	24.9	105.4	23.1	0.0	1.2	0.0	0.0	33.9
	25	0.0	0.1	1.6	0.0	0.2	1.7	3.8	89.5	1.1	1.3	1.3	29.5	115.8	25.1	0.0	1.1	0.0	0.0	33.9
	50	0.1	0.1	1.8	0.4	0.7	3.6	9.9	121.2	1.2	2.0	4.0	50.3	173.1	32.6	0.0	1.3	0.0	0.0	33.9

Table S4b. Continuation of RCF monomer concentration (μmol/g biomass) with pure solvents and aqueous mixtures (5-50 vol% water) of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA) and 1,4-dioxane (Diox).

IPA	0	0.0	0.0	1.1	0.0	0.0	0.9	1.4	50.7	0.4	0.5	0.0	13.6	51.1	17.6	0.0	0.0	0.0	0.0	33.9
	5	0.0	0.0	1.1	0.0	0.0	1.1	1.8	60.5	0.7	0.6	0.1	18.4	77.5	21.9	0.0	0.3	0.0	0.0	33.9
	15	0.0	0.1	1.4	0.0	0.1	1.3	2.6	69.9	1.0	1.0	0.7	23.2	93.7	26.5	0.0	0.2	0.0	0.0	33.9
	25	0.0	0.1	1.6	0.0	0.2	2.0	4.4	95.9	1.1	1.6	1.9	33.4	131.3	31.2	0.0	0.4	0.0	0.0	33.9
	50	0.0	0.1	2.0	0.2	0.7	4.1	10.5	139.0	1.1	2.2	4.9	55.0	207.2	39.1	0.0	0.6	0.0	0.0	33.9
IBA	0	0.0	0.0	1.0	0.0	0.0	0.8	1.2	51.9	0.5	0.5	0.0	13.2	54.4	16.2	0.0	0.2	0.0	0.0	33.9
	5	0.0	0.0	0.8	0.0	0.0	0.8	1.8	60.5	0.4	0.6	0.4	18.6	77.0	11.7	0.0	0.3	0.0	0.0	33.9
	15	0.0	0.0	1.0	0.0	0.0	1.0	2.8	77.4	0.6	0.9	1.1	26.6	106.4	13.9	0.0	0.2	0.0	0.0	33.9
	25	0.0	0.0	1.1	0.0	0.0	1.4	4.1	86.8	0.4	1.1	1.7	30.9	115.6	15.9	0.0	0.4	0.0	0.0	33.9
	50	0.0	0.0	0.6	0.0	0.1	2.5	11.2	152.9	0.3	1.4	1.8	62.7	219.5	18.6	0.0	0.6	0.0	0.0	33.9
Diox	0	0.0	0.1	1.1	0.1	0.0	0.6	4.3	30.4	0.2	0.0	0.6	10.8	32.2	1.4	0.0	0.0	0.0	0.0	33.9
	5	0.0	0.2	1.4	0.0	0.0	0.4	5.7	47.8	0.3	0.2	1.3	18.3	58.0	2.3	0.0	0.0	0.0	0.0	33.9
	15	0.0	0.2	1.4	0.0	0.2	0.3	5.5	46.0	0.7	0.1	0.0	19.4	59.2	2.0	0.0	0.0	0.0	0.0	33.9
	25	0.0	0.3	1.4	0.0	0.4	0.4	6.7	50.0	0.5	0.1	0.0	20.3	62.6	2.1	0.2	0.0	0.0	0.0	33.9
	50	0.0	0.2	1.2	0.0	0.7	1.0	9.1	59.9	0.4	0.7	0.0	28.9	78.5	4.9	0.0	0.4	0.0	0.0	33.9

Table S4c. Key for RCF monomer abbreviations

Abbreviation	Compound
H-Et	4-ethylphenol
H-Pr	4-propylphenol
H-PrOH	4-(3-hydroxypropyl)phenol
G-H	2-methoxyphenol
G-Me	4-methyl-2-methoxyphenol
G-Et	4-ethyl-2-methoxyphenol
G-Pr	4-propyl-2-methoxyphenol
G-PrOH	4-(3-hydroxypropyl)-2-methoxyphenol
S-H	2,6-dimethoxyphenol
S-Me	4-methyl-2,6-dimethoxyphenol
S-Et	4-ethyl-2,6-dimethoxyphenol
S-Pr	4-propyl-2,6-dimethoxyphenol
S-PrOH	4-(3-hydroxypropyl)-2,6-dimethoxyphenol
S-PrO*p*HB	*p*-hydroxybenzoate ester of S-PrOH
Me-*p*HB	methyl *p*-hydroxybenzoate
Et-*p*HB	ethyl *p*-hydroxybenzoate
Me-DHpCA	methyl 7,8-dihydro-*p*-hydroxycoumarate
Me-DHFA	methyl 7,8-dihydro-ferulate
DMB (internal standard)	1,2-dimethoxybenzene

Table S5. HSPs for the pure solvents and their aqueous mixtures (5-50 vol% water) used in the RCF experiments. HSPs for pure solvents are taken from Abbott and Hansen 2008[2] and those for solvent mixtures are obtained by the weighted average of HSPs of individual solvents based on their volume percentages.

Solvent system	δ_D	δ_P	δ_H
Ethylene Glycol (EG)	17	11	26
EG/water - 5 vol%	16.925	11.25	26.815
EG/water - 15 vol%	16.775	11.75	28.445
EG/water - 25 vol%	16.625	12.25	30.075
EG/water - 50 vol%	16.25	13.5	34.15
Methanol (MeOH)	14.7	12.3	22.3
MeOH/water - 5 vol%	14.74	12.485	23.3
MeOH/water - 15 vol%	14.82	12.855	25.3
MeOH/water - 25 vol%	14.9	13.225	27.3
MeOH/water - 50 vol%	15.1	14.15	32.3
Ethanol (EtOH)	15.8	8.8	19.4
EtOH/water - 5 vol%	15.785	9.16	20.545
EtOH/water - 15 vol%	15.755	9.88	22.835
EtOH/water - 75 vol%	15.725	10.6	25.125
EtOH/water - 50 vol%	15.65	12.4	30.85
Isopropanol (IPA)	15.8	6.1	16.4
IPA/water - 5 vol%	15.785	6.595	17.695
IPA/water - 15 vol%	15.755	7.585	20.285
IPA/water - 25 vol%	15.725	8.575	22.875
IPA/water - 50 vol%	15.65	11.05	29.35
Isobutanol (IBA)	15.1	5.7	15.9
IBA/water - 5 vol%	15.12	6.215	17.22
IBA/water - 15 vol%	15.16	7.245	19.86
IBA/water - 25 vol%	15.2	8.275	22.5
IBA/water - 50 vol%	15.3	10.85	29.1
1,4-dioxane (Diox)	17.5	1.8	9
Diox/water - 5 vol%	17.4	2.51	10.665
Diox/water - 15 vol%	17.2	3.93	13.995
Diox/water - 25 vol%	17	5.35	17.325
Diox/water - 50 vol%	16.5	8.9	25.65
Water	15.5	16	42.3

Correlation between RED and RCF Yield (wt% biomass)

It is well-established that the solubility of a polymer in a solvent can be characterized using the HSPs for both the polymer and the solvent by defining a spherical region in HSP space, centered on the HSPs of the polymer, such that solvents promoting polymer dissolution fall within this sphere (as shown in Fig. S5). The radius of the solubility sphere (R_0) depends on the polymer's solubility in the reference solvent systems. Solvents within the sphere can be identified by calculating the distance (R_a) between the polymer (*poly.)* and solvent (*solv.*) in $\delta_D - \delta_P - \delta_H$ space, as shown in equation S1.

$$R_a^2 = 4(\delta_D^{solv.} - \delta_D^{poly.})^2 + (\delta_P^{solv.} - \delta_P^{poly.})^2 + (\delta_H^{solv.} - \delta_H^{poly.})^2 \quad \text{(Eqn. S1)}$$

The solubility of a polymer can then be characterized by computing the Relative Energy Difference (RED), which is defined as the ratio of R_a to the interaction radius of the polymer (R_0),

$$\text{RED} = R_a/R_0 \quad \text{(Eqn. S2)}$$

A RED value greater than unity suggests that the polymer will not dissolve in a solvent, whereas a RED value less than unity suggests that it will dissolve in the solvent. RED calculations have been extensively used to understand and predict lignin behavior, including its fractionation, dissolution, and delignification in various solvents,[3-7] although HSPs for lignin can vary depending upon the feedstock. To determine if RED values can predict RCF yields, we calculated RED values for each solvent used for RCF by using the HSP of lignin reported by Hansen & Björkman, 1998[8] and Novo & Curvelo, 2019.[5] Table S6 shows RED values for each solvent and their aqueous mixtures based on these lignin HSPs. Fig. S5 shows corresponding solubility spheres for these different sets of lignin HSPs; no clear correspondence between points within the sphere and the experimental RCF yields is observed.

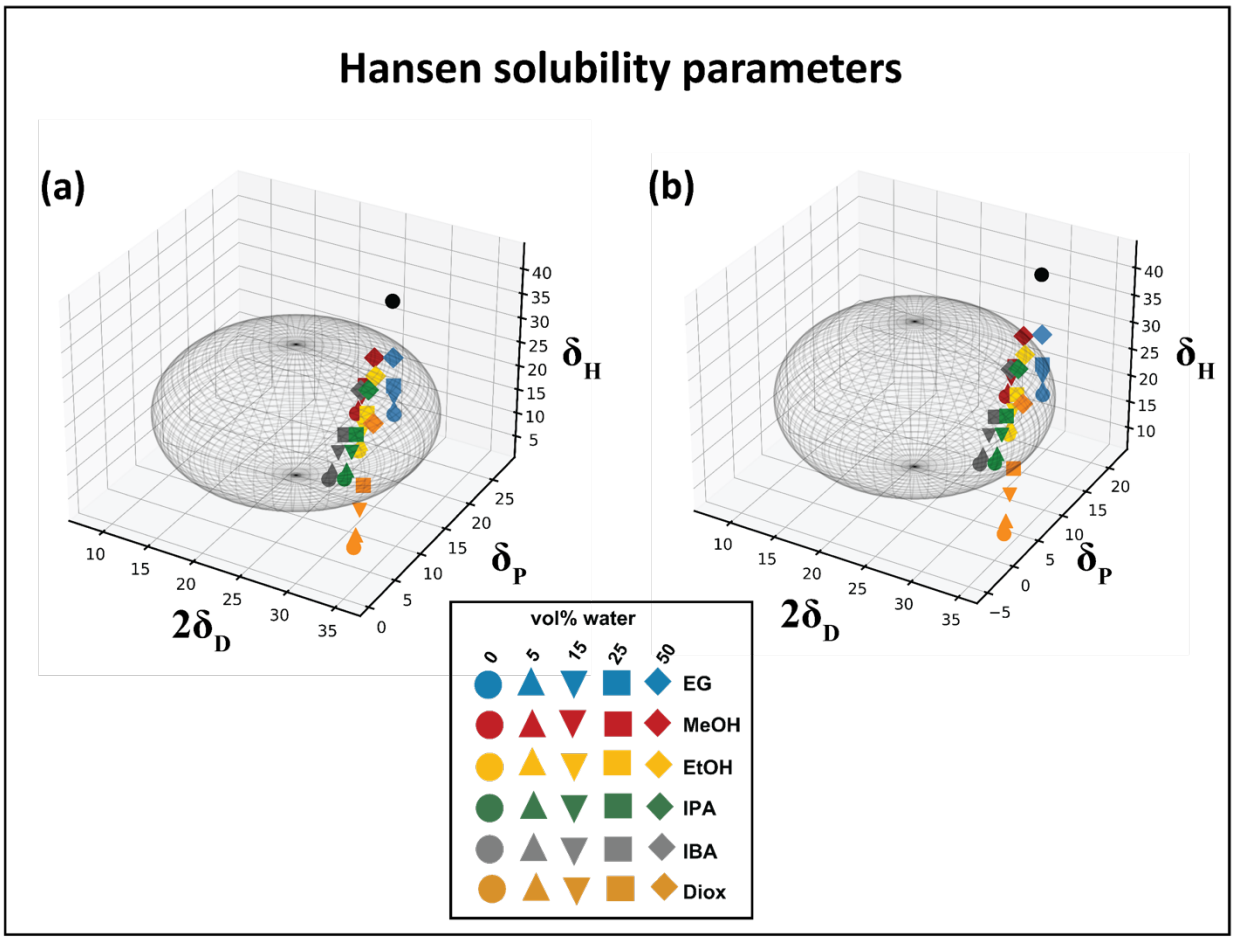

Fig. S5. Hansen solubility parameters sphere for lignin: (a) using lignin HSP values reported by Hansen & Björkman, 1998.[8] (b) using lignin HSP values reported by Novo & Curvelo, 2019.[5]

Table S6. RED values for all pure solvents and their aqueous mixtures (5-50 vol% water), calculated using the Eqns S1 and S2.

Solvent/Solvent mixtures	RED (Hansen & Björkman[a])	RED (Novo & Curvelo[b])
Ethylene Glycol (EG)	1.00	0.74
EG/water - 5 vol%	1.05	0.78
EG/water - 15 vol%	1.14	0.87
EG/water - 25 vol%	1.24	0.97
EG/water - 50 vol%	1.51	1.24
Methanol (MeOH)	1.13	1.03
MeOH/water - 5 vol%	1.15	1.03
MeOH/water - 15 vol%	1.22	1.06
MeOH/water - 25 vol%	1.27	1.10
MeOH/water - 50 vol%	1.50	1.28
Ethanol (EtOH)	0.99	0.85
EtOH/water - 5 vol%	1.00	0.84
EtOH/water - 15 vol%	1.04	0.84
EtOH/water - 75 vol%	1.11	0.89
EtOH/water - 50 vol%	1.37	1.12
Isopropanol (IPA)	1.07	0.94
IPA/water - 5 vol%	1.05	0.90
IPA/water - 15 vol%	1.04	0.85
IPA/water - 25 vol%	1.08	0.84
IPA/water - 50 vol%	1.31	1.03
Isobutanol (IBA)	1.17	1.05
IBA/water - 5 vol%	1.15	1.00
IBA/water - 15 vol%	1.12	0.94
IBA/water - 25 vol%	1.14	0.92
IBA/water - 50 vol%	1.33	1.06
1,4-dioxane (Diox)	1.25	1.21
Diox/water - 5 vol%	1.16	1.11
Diox/water - 15 vol%	1.03	0.91
Diox/water - 25 vol%	0.96	0.77
Diox/water - 50 vol%	1.08	0.78
Water	2.08	1.83

[a]Lignin HSP (($\delta_D, \delta_P, \delta_H$) is 21.9, 14.1, 16.9 and R_0= 13.7) taken from Hansen & Björkman, 1998.[8]

[b]Lignin HSP (($\delta_D, \delta_P, \delta_H$) is 21.42, 8.57, 21.80 and R_0= 13.56) taken from Novo & Curvelo, 2019.[5]

RED values for all solvents/mixtures summarized in Table S6 were used to further quantify the correlation between RED values and RCF yield (wt% biomass). Fig. S6 shows weak linear correlations between RED values and RCF yields with Pearson correlation coefficients of 0.60 for RED values based on the Hansen & Björkman, 1998 lignin HSPs[8] and of 0.23 for RED values based on the Novo & Curvelo, 2019 lignin HSPs;[5] perfect linear correlation corresponds to a value of 1.0. These results indicate that RED values alone are poor predictors of RCF yields, at least when using reported lignin HSPs.

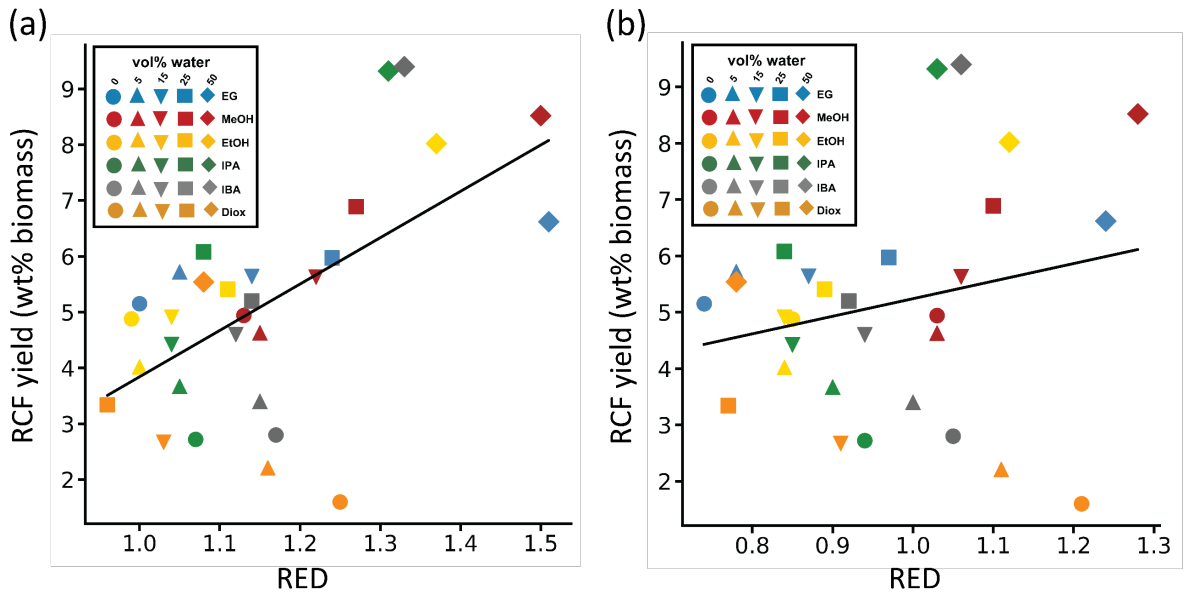

Fig. S6 RED versus RCF yield (wt% biomass) in all pure solvents and their aqueous mixtures (5-50 vol% water). The dashed line is the best-fit line between these two variables. Figure S6a and S6b represent the RED values based on lignin HSPs from Hansen & Björkman, 1998 and Novo & Curvelo, 2019, respectively.[5,8]

We further tried to optimize RED values based on Hansen & Björkman lignin HSPs to see if alternative lignin HSPs could achieve a Pearson correlation coefficient close to unity. To do so, we numerically solved for the set of HSPs that lead to the highest linear correlation between resulting RED values and experimental RCF yields. The optimal values lead to a Pearson correlation coefficient of 0.905; however, all the RED values were higher than unity, which contradicts the typical interpretation of these values (discussed above). We alternatively enforced a constraint that RED values had to be less than 1, leading to a lower Pearson correlation coefficient

(0.83). This overall poor correlation results suggests that although RED values correlate with delignification yield, these values are insufficient to predict RCF yields, motivating the use of alternative regression models to better understand and quantify the correlation between RCF yield and solvent HSPs.

Multidescriptor correlation between experimental RCF yield (wt% biomass) and HSPs

To explore the contributions of HSPs of solvents or their aqueous mixtures to the experimental RCF yield (wt% biomass), we fit a multiple linear regression model, as shown in equation (S3), using HSPs as dependent variables to predict the experimental yield:

$$yield_{pred} = A + B(\delta_D) + C(\delta_P) + D(\delta_H) \quad \text{(Eqn. S3)}$$

All HSPs were first normalized between 0 and 1 using the minimum and maximum value of each HSP in the data set (described below) so that the magnitude of regression coefficients can be compared to determine the importance of each HSP to model predictions.

Fig. S7 compares the RCF yield (wt% biomass) predicted using the linear regression model (Eqn S3) with the experimental RCF yield (wt% biomass) for all solvents/mixtures used in the RCF process. Model coefficients along with the coefficient of determination (R^2) and RMSE values are shown in Fig. S7. δ_H (strength of hydrogen bonding interactions) has the largest weight in the linear correlation model. However, the moderate accuracy (R^2 = 0.84 and RMSE = 0.77) suggests a need for further improvement in the model prediction. In addition, the higher Spearman rank correlation coefficient, ρ (where a value of indicates a perfect monotonic, but not necessarily linear, relationship) of 0.96 for this model suggest that the relationship between experimental RCF yield and HSPs for solvents may be better captured using a non-linear modeling approach.

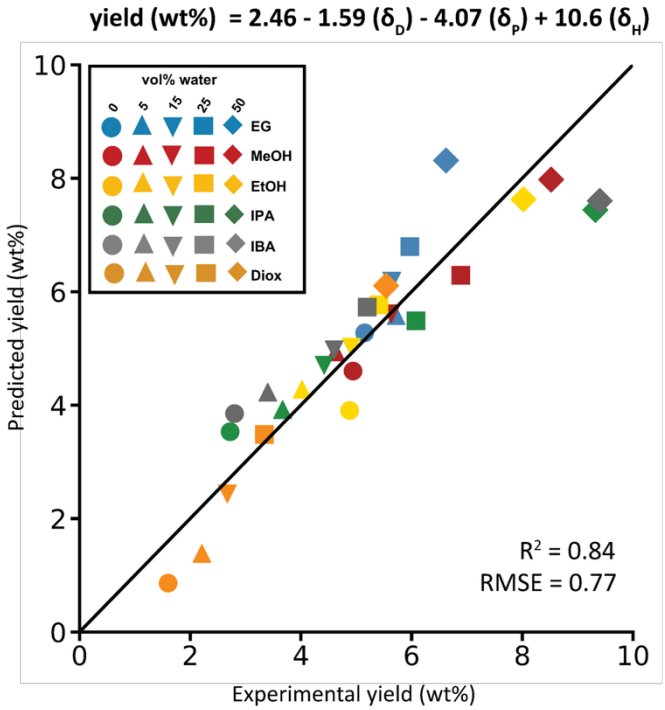

Fig. S7 Predicted RCF yield (wt% biomass) calculated using the three HSPs correlation model plotted against the experimental RCF yield (wt% biomass) for all pure solvents and their aqueous mixtures (5-50 vol% water) used in RCF process (also listed in Table S2).

Procedure for Normalizing Descriptors (HSPs) used in Correlation Model

The values for HSPs ($\delta_D, \delta_P, \delta_H$) are normalized between 0 and 1 using the following procedure:

$$\tilde{x} = \frac{x - \min(x)}{\max(x) - \min(x)} \quad \text{(Eqn. S4)}$$

where x is the original HSP value and $\tilde{x}$ is the normalized HSP value. Normalizing the HSP values allows us to compare the coefficients in the regression model to determine the contribution of each model parameter to the predicted yield.

Non-linear regression modeling using ALAMO

ALAMO (Automated Learning of Algebraic Models)[9-11] is a regression and classification model learning methodology to construct simple, yet accurate models based on data from experiments, simulations or other. It utilizes a minimal set of sample points to build these models, making it useful for ensuring that the resulting model is both accurate and as simple as possible. ALAMO provides the optimized prediction model by using different modelers such as AICc, BIC, Cp, etc. The R^2 and RMSE values in linear correlation model suggests the need for further improvement in the model predictive accuracy (described in Fig. S7). To improve the model's predictive accuracy, we next fit a quadratic regression model by using ALAMO to relate HSPs to experimental monomer yields as described by the following equation (S5):

$$yield = \beta_0 + \beta_1\delta_D + \beta_2\delta_P + \beta_3\delta_H + \beta_4\delta_D^2 + \beta_5\delta_P^2 + \beta_6\delta_H^2 \quad \text{(Eqn. S5)}$$

where $\beta_0 - \beta_6$ are the regression coefficients.

Fig. S8 compares the experimental RCF monomer yield (wt% biomass) and the yield calculated using quadratic regression model . The optimal model results in R^2 value of 0.85 and RMSE of 0.74. The comparison of regression coefficients in the quadratic regression model also indicate the largest weight of δ_H (hydrogen bonding interactions) in the model prediction, in agreement with the linear regression model. However, the lower model accuracy suggests the need for further improvement in the model prediction, motivating the additional of interaction terms and resulting in the final quadratic regression with interaction terms model described in the main text.

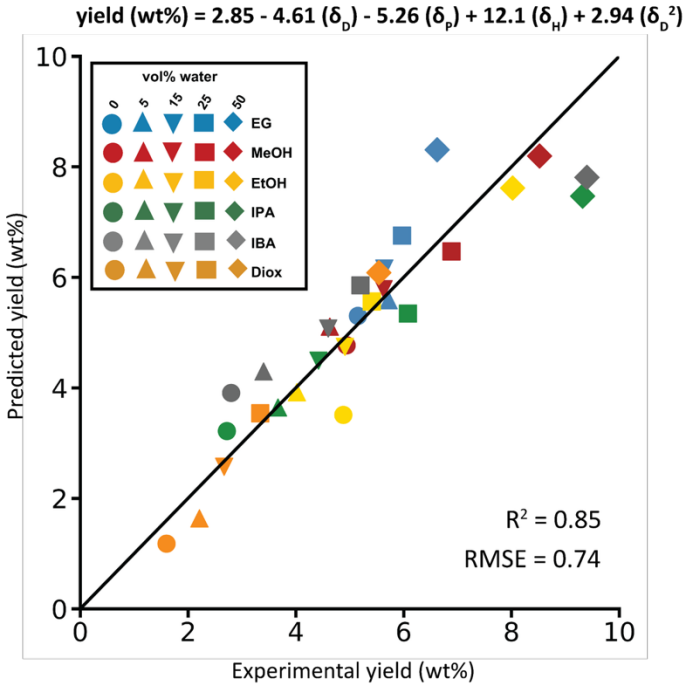

Fig. S8. Predicted RCF monomer yield (wt% biomass) calculated using quadratic regression model plotted against the experimental RCF yield (wt% biomass) for all pure solvents and their aqueous mixtures (5-50 vol% water) listed in Table S2.

Comparison of alternative models: Model performance and complexity

Adding more parameters to a regression model usually improves its ability to predict experimental outcomes. However, the simplest model that accurately predict the realistic behavior is most meaningful. When comparing models, it is important to determine whether the improved predictions from additional parameters are statistically significant or introduce unnecessary complexity. Moreover, models with excessive parameters may perform poorly on unseen data, as they lack the robustness needed for generalization. This trade-off between predictive accuracy and model complexity can be evaluated using information criteria such as the Bayesian Information Criterion (BIC), corrected Akaike Information Criterion (AICc) and Mallows' Cp (Cp).[12-14] These metrics provide a systematic framework for comparing alternative models by balancing accuracy and simplicity and are defined in equations S6, S7 and S8:

$$BIC = k\ln(n) - 2\ln(\hat{L}) \quad \text{(Eqn. S6)}$$

$$AICc = 2k - 2\ln(\hat{L}) + \frac{2k^2+2k}{n-k-1} \quad \text{(Eqn. S7)}$$

$$C_p = \frac{SSE}{S^2} - n + 2k \quad \text{(Eqn. S8)}$$

k is the number of model parameters, n is the number of data points being fit, $\hat{L}$ is the maximum value of model's log-likelihood function, SSE is sum squared error ($\sum_{i=1}^{n}(x_i - \hat{x})^2$ with x_i observed value and $\hat{x}$ predicted value, and S^2 is residual mean squared error. In model selection, the model with the smallest values of BIC, AICc and C_p are typically preferred. The AICc, BIC and C_p values for three different correlation models are summarized in Table S7, along with their model accuracy metrics, R^2 and RMSE. From Table S7, we find that the quadratic regression with interaction terms model (as described in Eqn. 3 of the main text) with four parameters has the lowest AICc, BIC and C_p values, along with improved R^2 and RMSE values, indicating that model is both statistically significant and predictive.

Table S7. Summary of model performance and complexity: AICc, BIC, C_p, R^2, RMSE and model size.

Model	Number of Parameters	AICc	BIC	C_p	R^2	RMSE
Linear	4	-6.04	-2.03	-4.19	0.842	0.771
Quadratic	5	-5.01	-0.508	-3.27	0.852	0.747
Quadratic with Interaction terms	**4**	**-25.4**	**-21.4**	**-12.7**	**0.92**	**0.56**

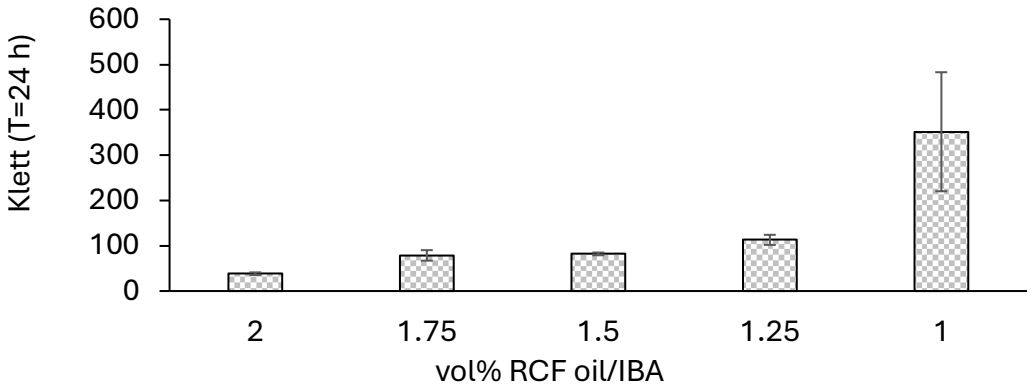

Fig. S9 Growth of *N. aromaticivorans* strain PDC in 1-2 vol% RCF oil in IBA. Culture conditions: SMB media supplemented with glucose (2 g/L) and 2 vol% RCF oil in solvent, 24 h, 30 °C, 200 rpm. Standard error was determined from n = 3 technical replicates.

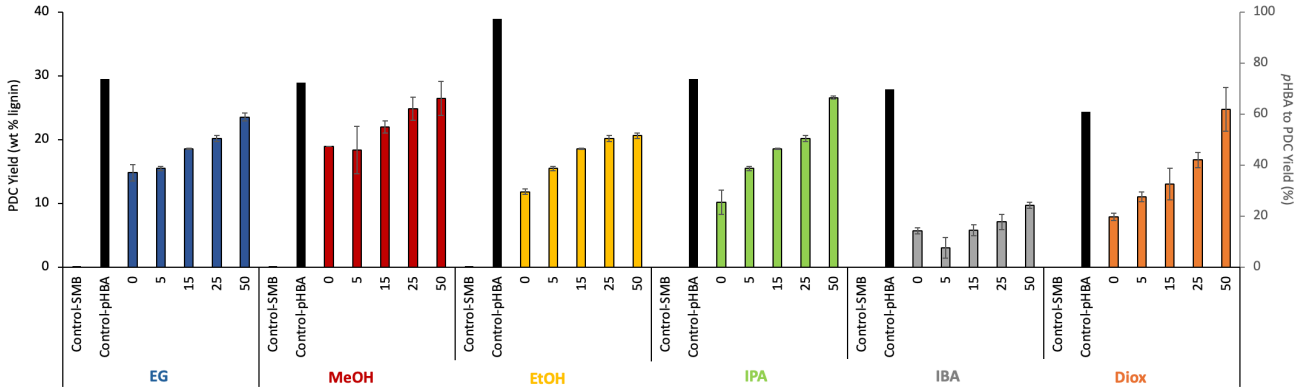

Fig. S10. PDC yields produced by a strain of *N. aromaticivorans* DSM12444 from the RCF aromatics on a lignin basis from pure solvents of ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), isobutanol (IBA), and 1,4-dioxane (Diox). Culture conditions: SMB media supplemented with glucose and 2 vol% RCF oil in solvent, 24 h, 30 °C, 200 rpm.

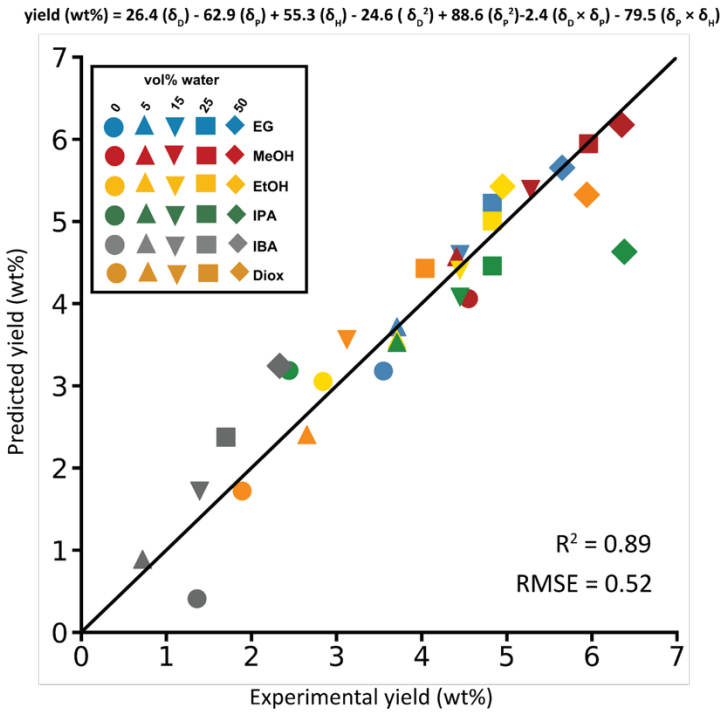

Fig. S11 Predicted PDC yield (wt% biomass) calculated using quadratic regression model with interaction terms model plotted against the experimental PDC yield (wt% biomass) for pure solvents and their aqueous mixtures (5-50 vol% water) listed in Table S2. The optimized equation for quadratic regression model with interaction terms, is displayed at the top of the figure.

Technoeconomic Analysis

Process Data

Table S8. Feedstock composition

Component	wt% (dry basis)
Glucan	46.6%
Xylan	16.2%
Arabinan	0.6%
Mannan	2.9%
Galactan	0.8%
Sucrose	0.5%
Acetate	4.3%
Extractives	5.8%
Lignin	24%
Ash	0.3%
Total	**100%**
Moisture	16.7%

Table S9a. Key process design data for each solvent system

Component	Pure Solvent System					
	MeOH	EtOH	IPA	IBA	EG	Diox
RCF:						
Reaction Condition (°C, bar)	200, 60	200, 54	200, 59	200, 46	200, 7	200, 30
*Dry biomass: Solvent (mass ratio)	1 : 17.251	1 : 17.190	1 : 17.102	1 : 17.473	1 : 24.183	1 : 22.505
Dry biomass: Catalyst (mass ratio)	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056
Catalyst lifetime (yr)	1	1	1	1	1	1
PDCP:						
Reaction Condition (°C, atm, hr)	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24
**Monomer-to-PDC yield (%)	92.9	57.9	61.0	48.7	68.2	118.2***
HYD:						
Glucose concentration in hydrolysate (g/L)	112	112	112	112	112	112
Xylose concentration in hydrolysate (g/L)	42	42	42	42	42	42
FERM Area:						
Glucose conversion to ethanol (%)	100	100	100	100	100	100
Xylose conversion to ethanol (%)	62	62	62	62	62	62

*Estimated based on experimental value of 30 mL, and density of solvent and water. Biomass value is 1.377 g

**Estimated based on biomass-to-monomer yield and biomass-to-PDC yield from the experimental data

***Since the PDC yield was higher than the monomer yield due to the possible conversion of other compounds to PDC by the microbe *N.aromaticivorans*, we assume 100% monomer conversion, with the extra conversion accounted for in carbohydrate conversions

Table S9b. Key process design data for each solvent/water mixture

Component	50 vol% Solvent/Water System					
	MeOH/water	EtOH/water	IPA/water	IBA/water	EG/water	Diox/water
RCF:						
Reaction Condition (°C, bar)	200, 48	200, 47	200, 46	200, 44	200, 21	200, 30
*Dry biomass: Solvent (mass ratio)	1 : 19.513	1 : 19.488	1 : 19.444	1 : 19.630	1 : 22.985	1 : 22.146
Dry biomass: Catalyst (mass ratio)	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056	1 : 0.056
Catalyst lifetime (yr)	1	1	1	1	1	1
PDCP:						
Reaction Condition (°C, atm, hr)	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24	30, 1, 24
**Monomer-to-PDC yield (%)	74.7	61.8	68.6	25.0	85.5	108.0***
HYD:						
Glucose concentration in hydrolysate (g/L)	112	112	112	112	112	112
Xylose concentration in hydrolysate (g/L)	42	42	42	42	42	42
FERM:						
Glucose conversion to ethanol (%)	100	100	100	100	100	100
Xylose conversion to ethanol (%)	62	62	62	62	62	62

*Estimated based on experimental value of 30 mL, and density of solvent and water. Biomass value is 1.377 g

**Estimated based on biomass-to-monomer yield and biomass-to-PDC yield from the experimental data

***Since the PDC yield was higher than the monomer yield due to the possible conversion of other compounds to PDC by the microbe *N.aromaticivorans*, we assume 100% monomer conversion, with the extra conversion accounted for in carbohydrate conversions

Process Description

We use Fig.S12 to show how the RCF and MNP block connection to the process configuration in ASPEN. In subsequent figures, we only show the process configuration and only highlight the major modifications.

Fig.S12 shows the process configuration of the RCF and MNP blocks simulated in ASPEN PLUS for MeOH system. 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 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 methanol stream pressure is increased using a pump and preheated using the vapor streams from the flash tanks using heat exchangers (HX1,2,3) and finally heated to meet RCF reactor conditions. The hydrogen stream is compressed using a multi-stage compressor (CPR) equipped with electric heaters to meet reactor conditions.

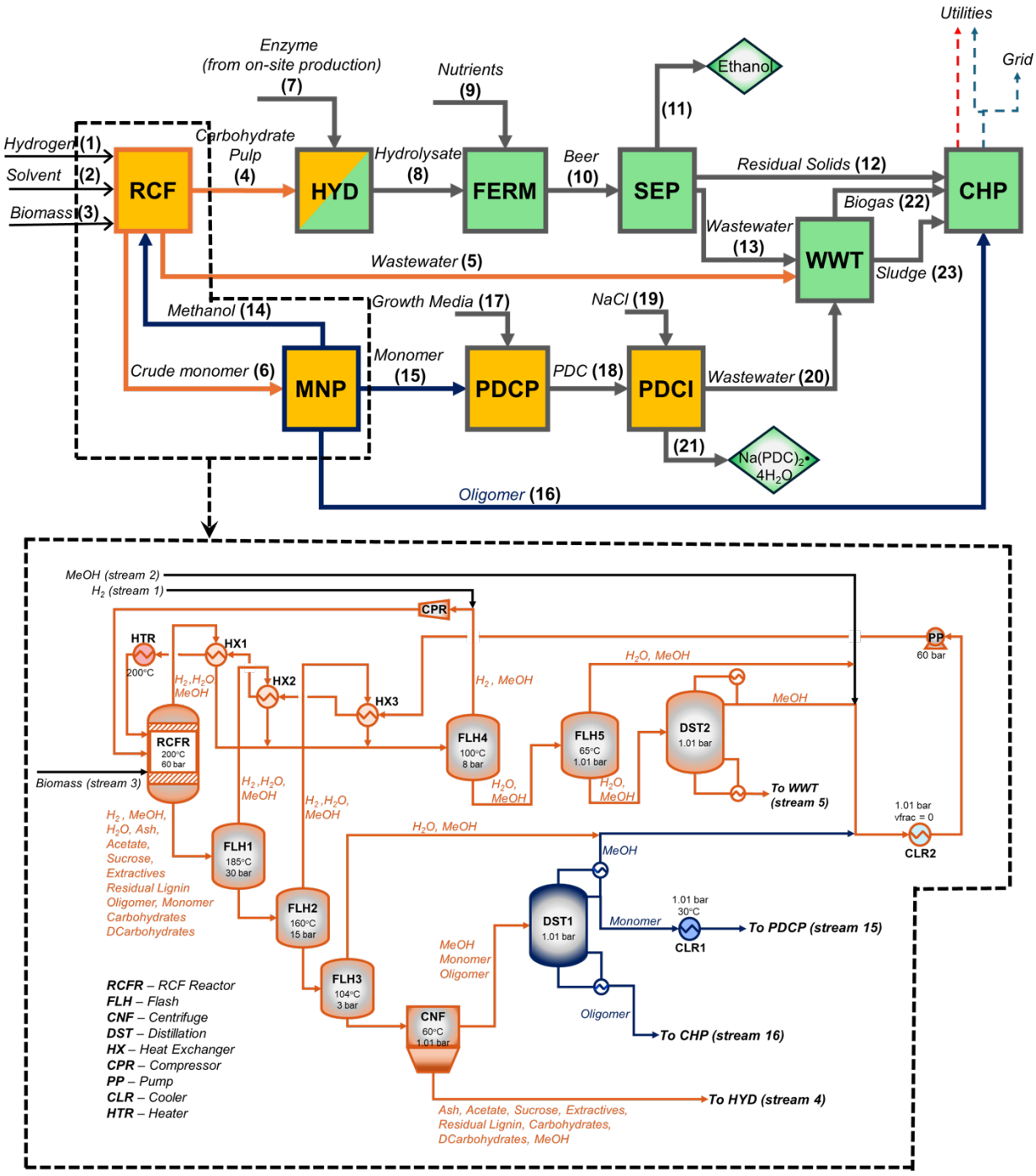

Fig. S12. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the MeOH system (adapted and modified from Sener et al. 2025)[15]

Fig.S13 shows the process configuration of the RCF and MNP blocks simulated in ASPEN PLUS for EtOH system. The process configuration follows the same as the MeOH system with main differences being the process parameters. Here, the RCFR operates at 54 bar. Due to the higher boiling point of ethanol relative to methanol, FLH1 operates at a slightly lower pressure of 23 bar. FLH2 operates at 166°C and 14 bar while FLH3 operates at 111°C and 3.03 bar. DST2 is operated in vacuum at a pressure of 0.8 atm (0.811 bar) to reduce heat demands when approaching azeotropic point of ethanol/water.

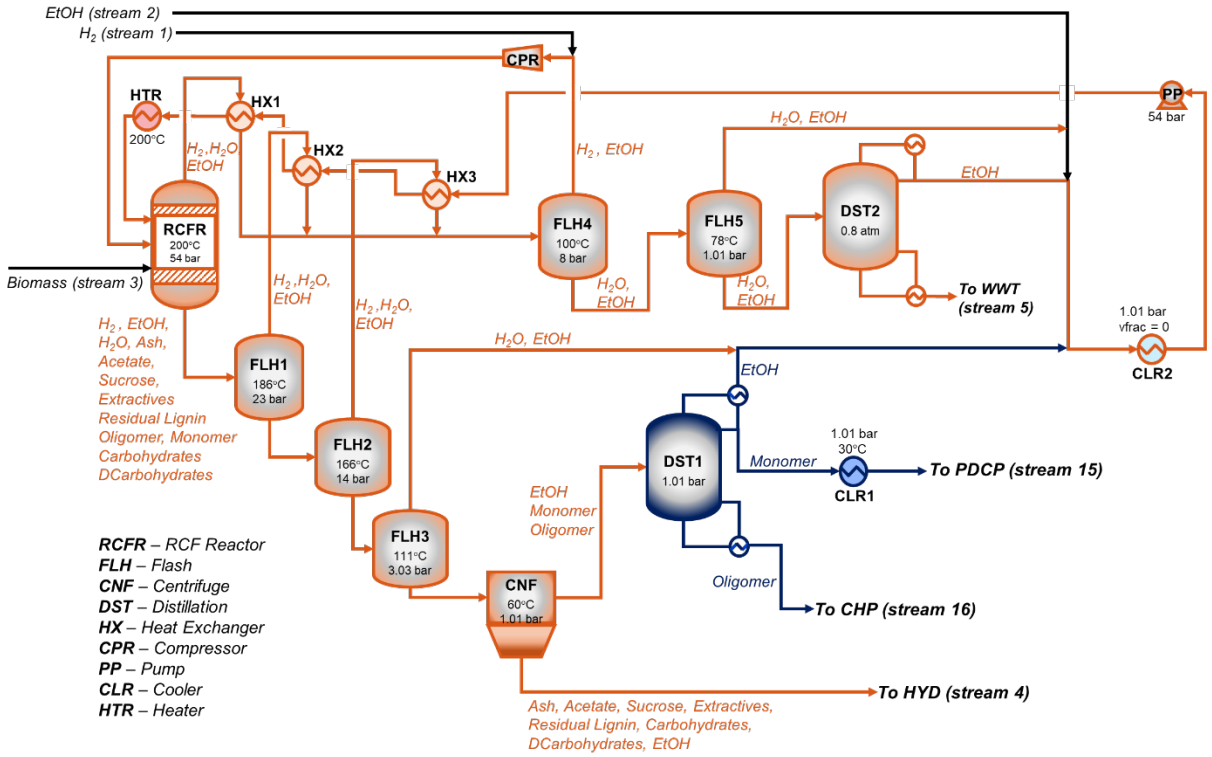

Fig. S13. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the EtOH system

Fig.S14 shows the process configuration of the RCF and MNP blocks simulated in ASPEN PLUS for IPA base system. Here, we make modifications to the flash units (FLH1-3) as well as DST2 being operated in vacuum.

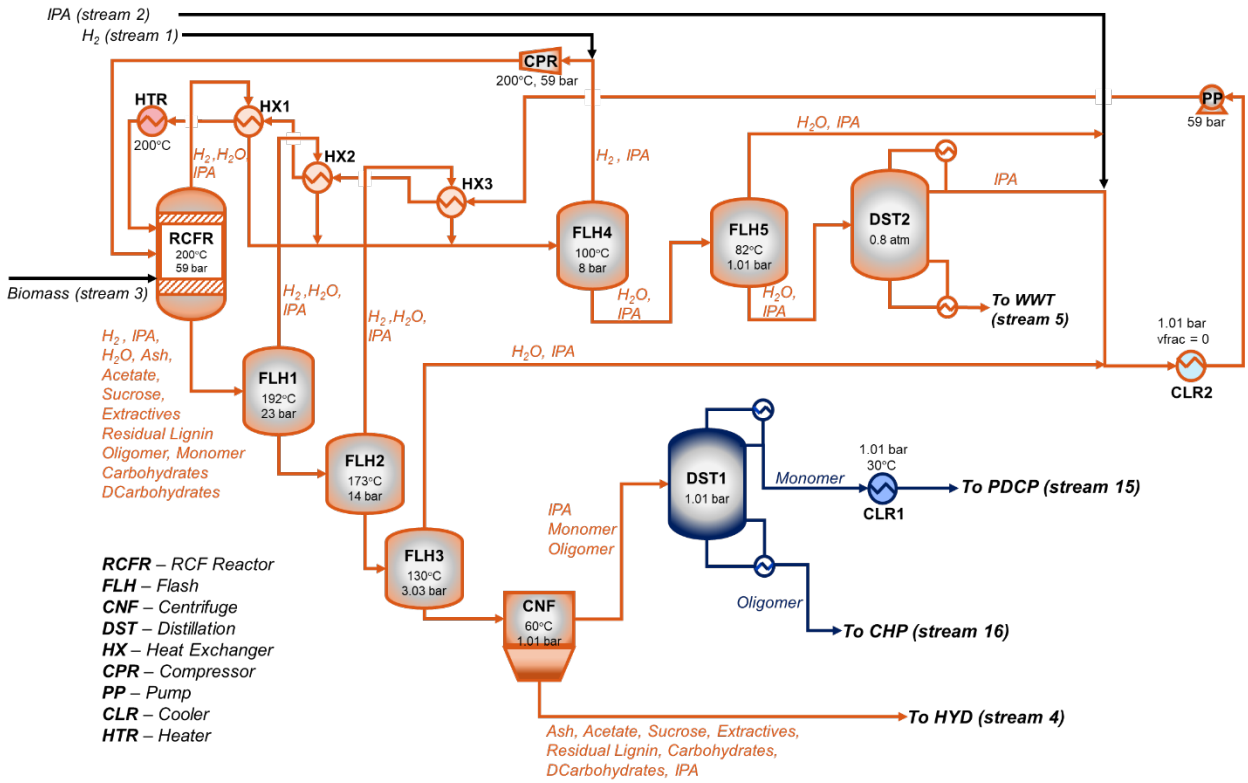

Fig. S14. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the IPA system

Fig.S15 shows the process configuration of the RCF and MNP blocks simulated in ASPEN PLUS for IBA base system. Here, the main modifications include operating DST2 at 0.5 bar while we use two distillation columns (DST1 and DST3) in series for monomer purification due to the higher boiling point of IBA. Also, due to the relative lower pressure of the RCF reactors, the number of flash units reduces to four instead of five in previous configurations.

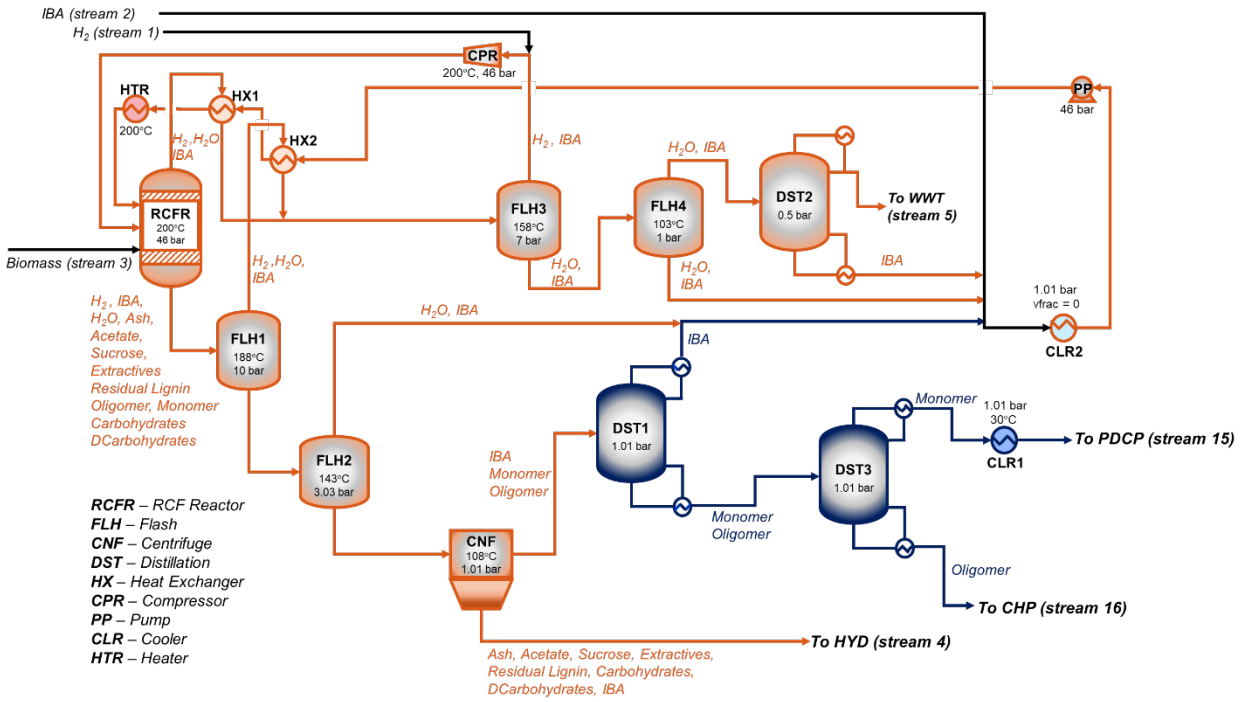

Fig. S15. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the IBA system

Fig.S16 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for EG base system. Here, we operate DST1 under moderate vacuum while DST2 operates under strong vacuum to help reduce heating requirements.

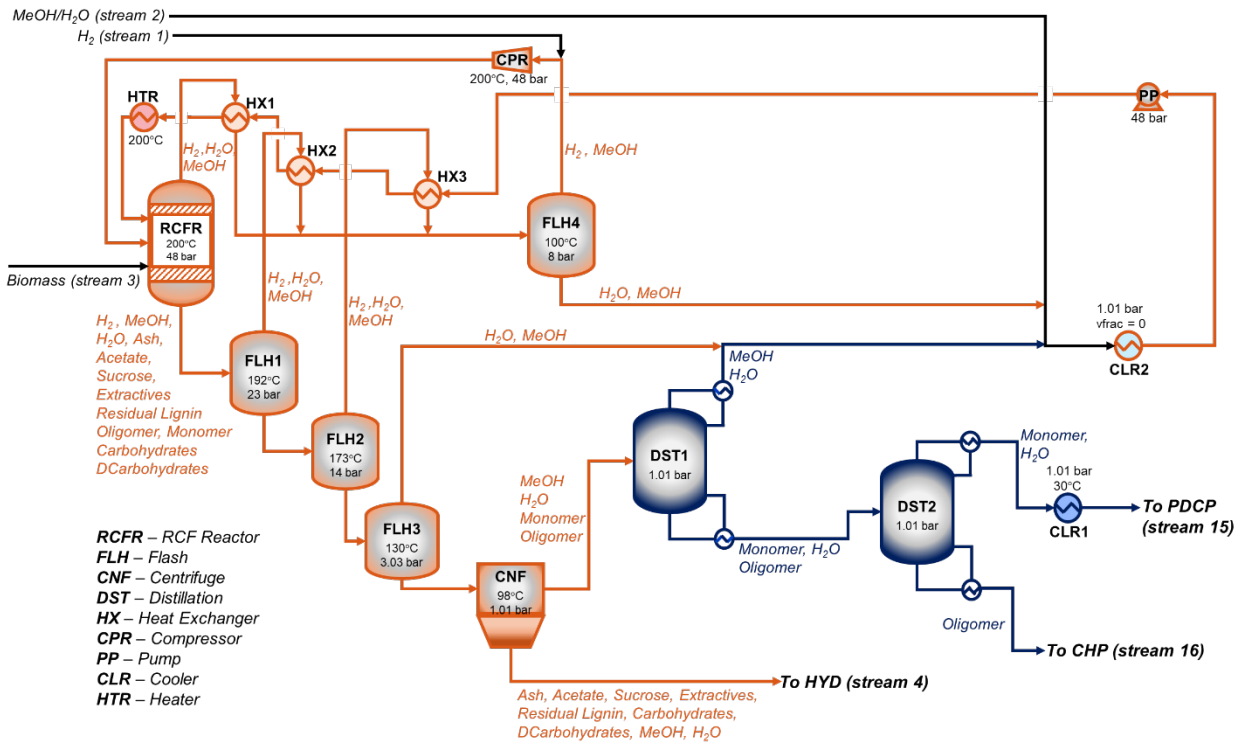

Fig. S16. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the EG system

Fig.S17 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for Diox pure system. Here, major modifications include flash operating conditions and operating DST2 under vacuum.

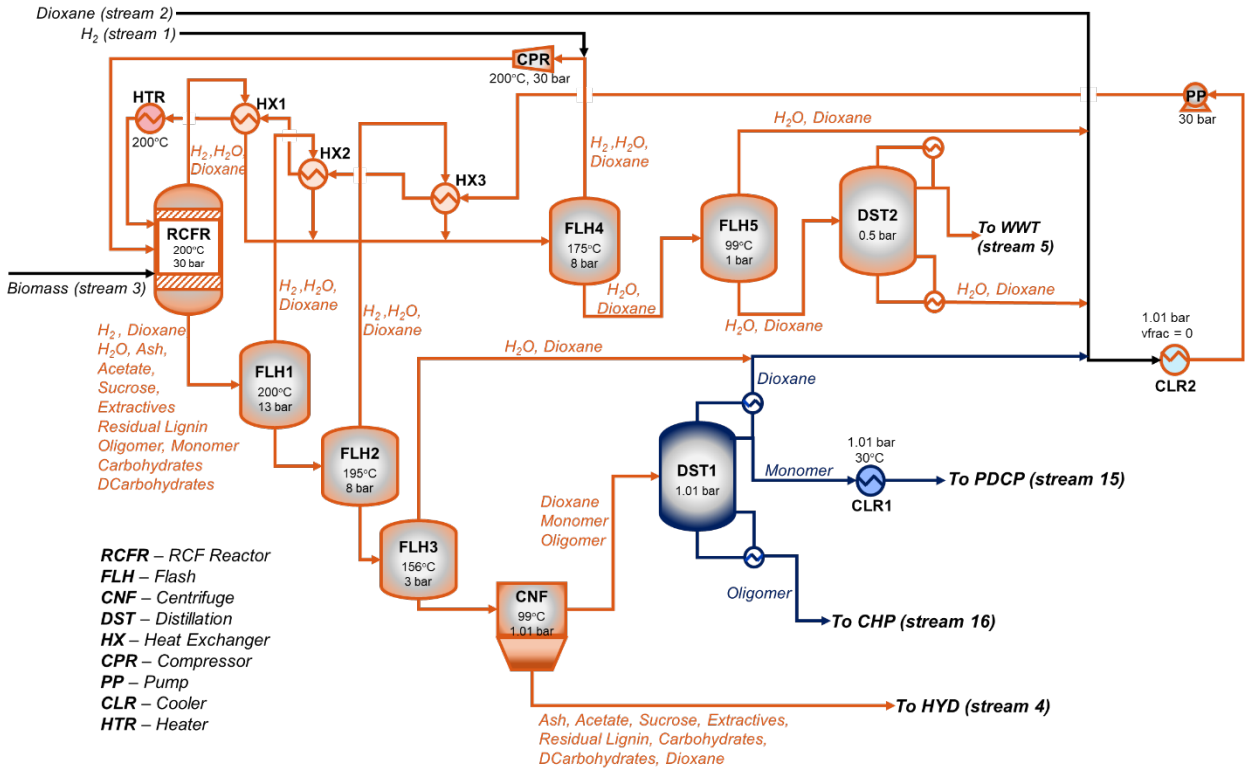

Fig. S17. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the Diox system

Fig.S18 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% MeOH/water system. Here, due to the presence of water, we use two distillation columns for monomer purification, with the first column, operated with a partial condenser allowing for methanol and water recycling, while the second column is operated with a total condenser.

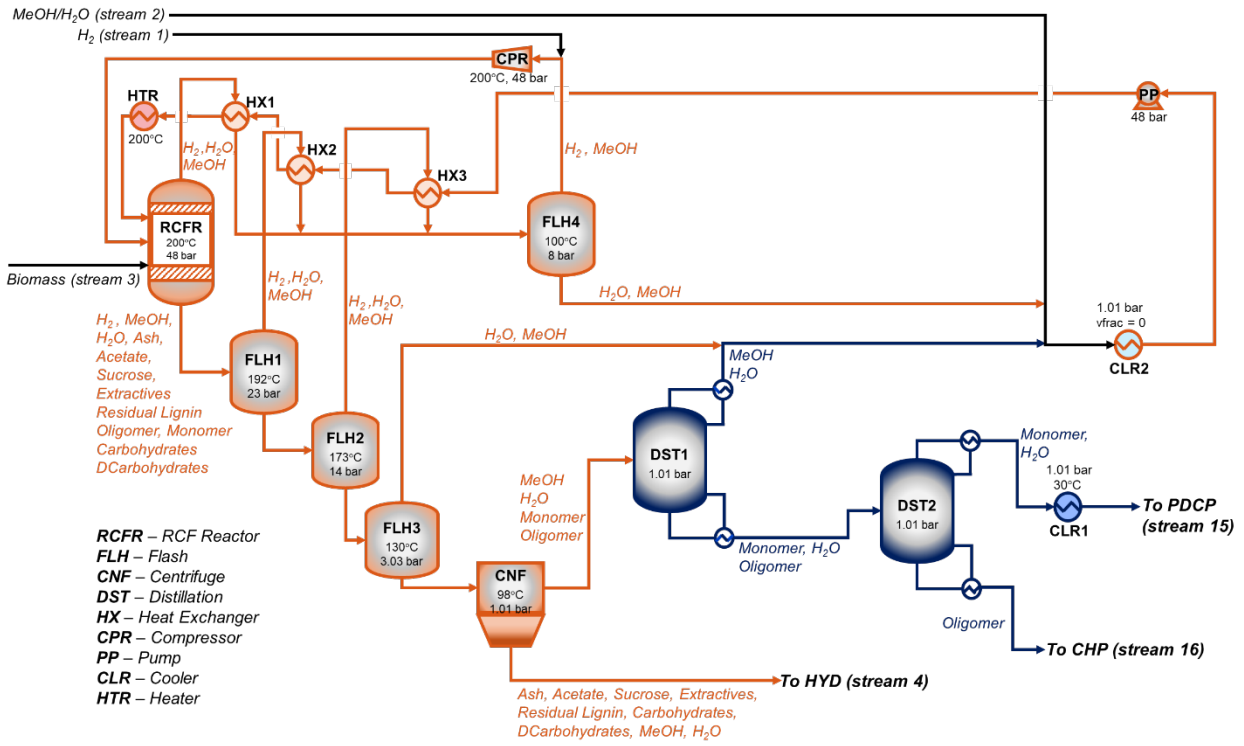

Fig. S18. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the MeOH/water system

Fig.S19 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% EtOH/water system. Here, the process is similar to the MeOH/water system with main modifications being the operating conditions of the flash units due to the lower pressure in RCF reactors.

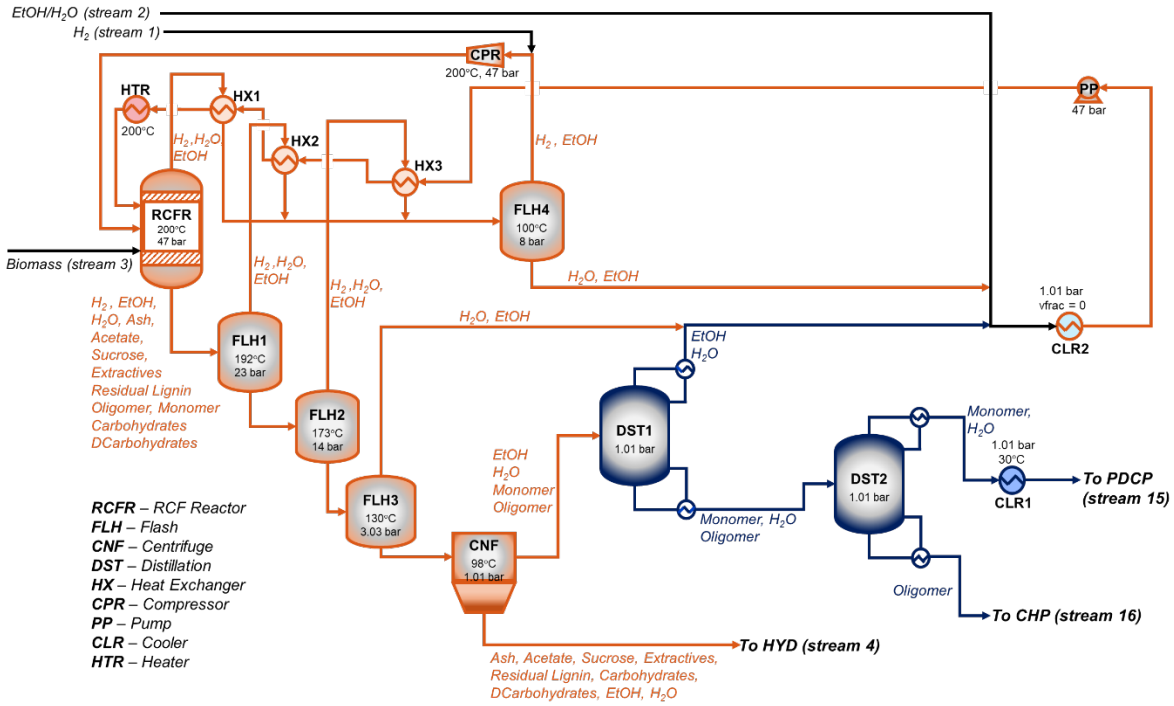

Fig. S19. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the EtOH/water system

Fig.S20 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% IPA/water system. Due to the closer boiling of isopropanol and water, we initially flash the reactor products at higher temperatures and lower pressure to evaporate most of the solvent and water. The remaining solvent and water is recovered using a partial condenser in DST1.

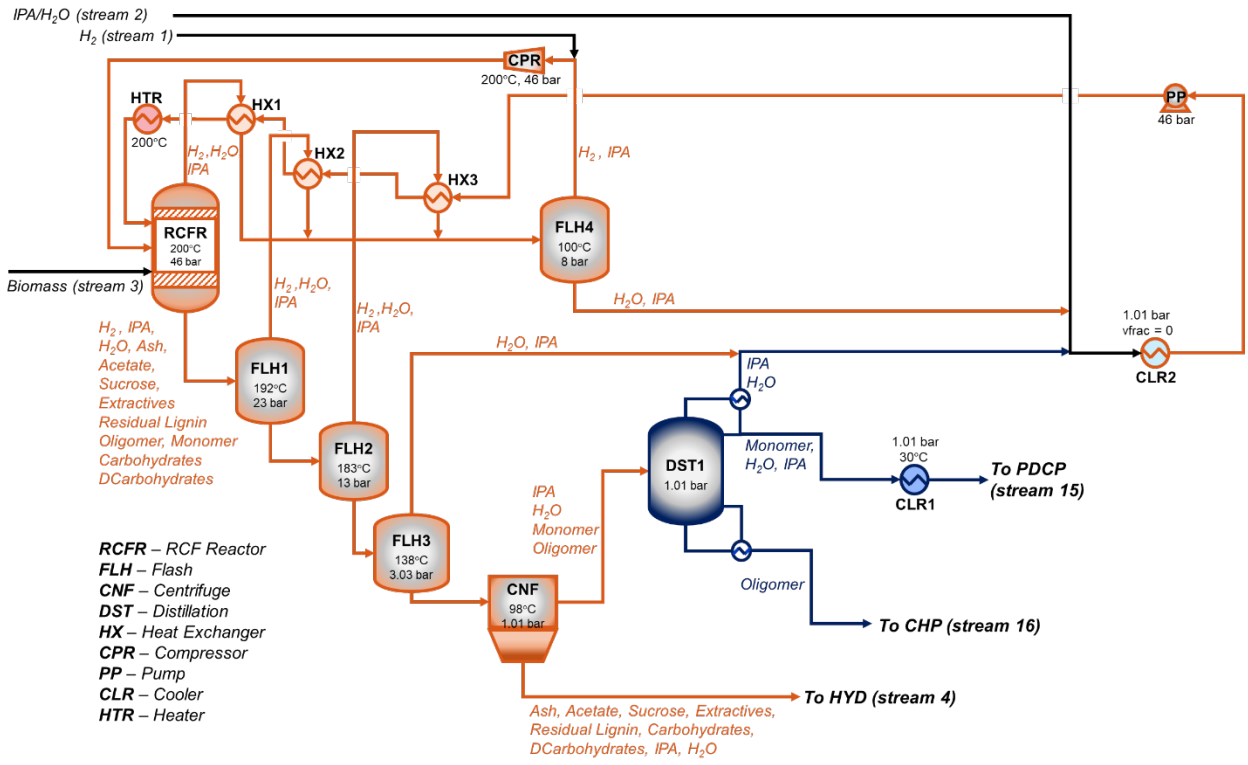

Fig. S20. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the IPA/water system

Fig.S21 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% IBA/water system. Here, due to the higher boiling point of Isobutanol compared to water, we use two distillation columns for monomer separation.

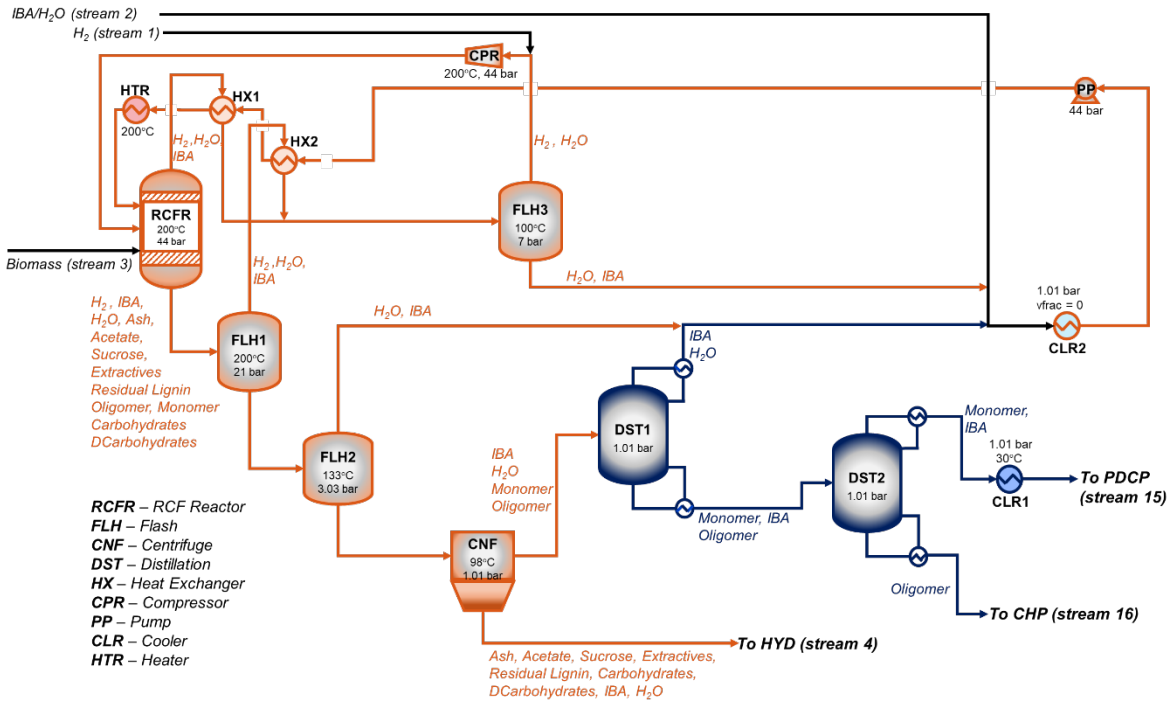

Fig. S21. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the IBA/water system

Fig.S22 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% EG/water system. Here, due to the high boiling point and low vapor pressure of ethylene glycol, we use two distillation columns operated under vacuum to help reduce heat requirements for solvent recovery.

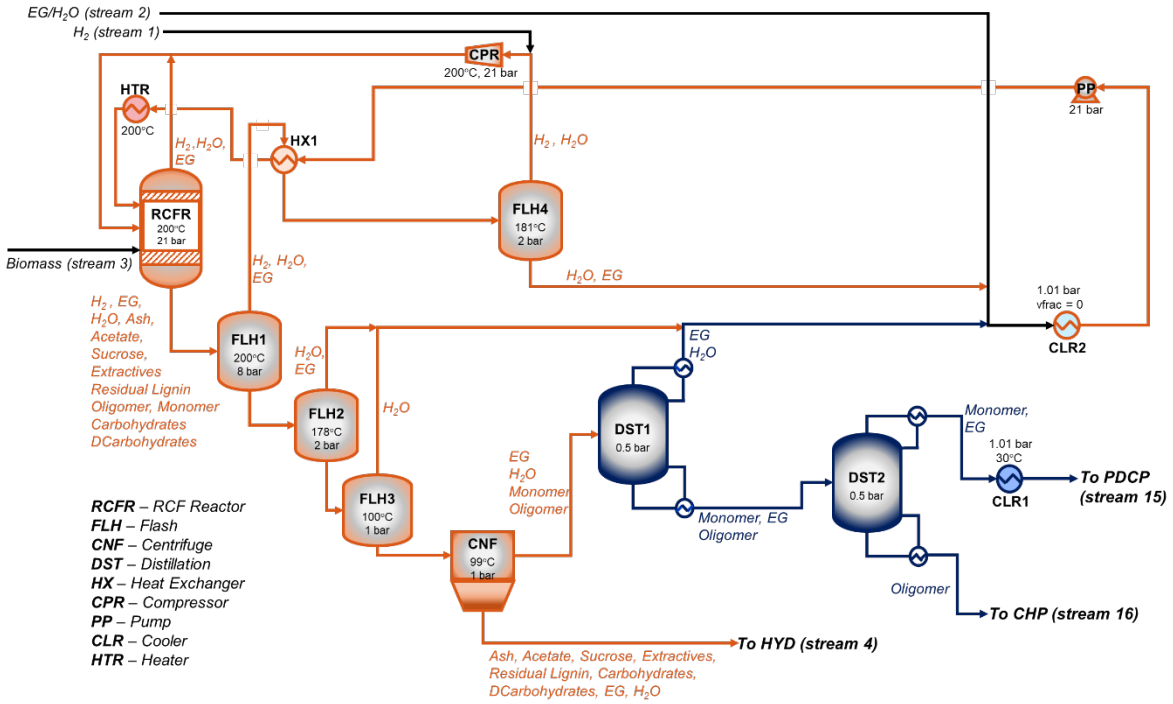

Fig. S22. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the EG/water system

Fig.S23 shows the process configuration of the RCF and MNP areas simulated in ASPEN PLUS for 50 vol% Diox/water system . Here, due to close boiling points of dioxane and water, most of the solvent-water are flashed using FLH1,2. Hence only a single distillation column is needed for monomer recovery.

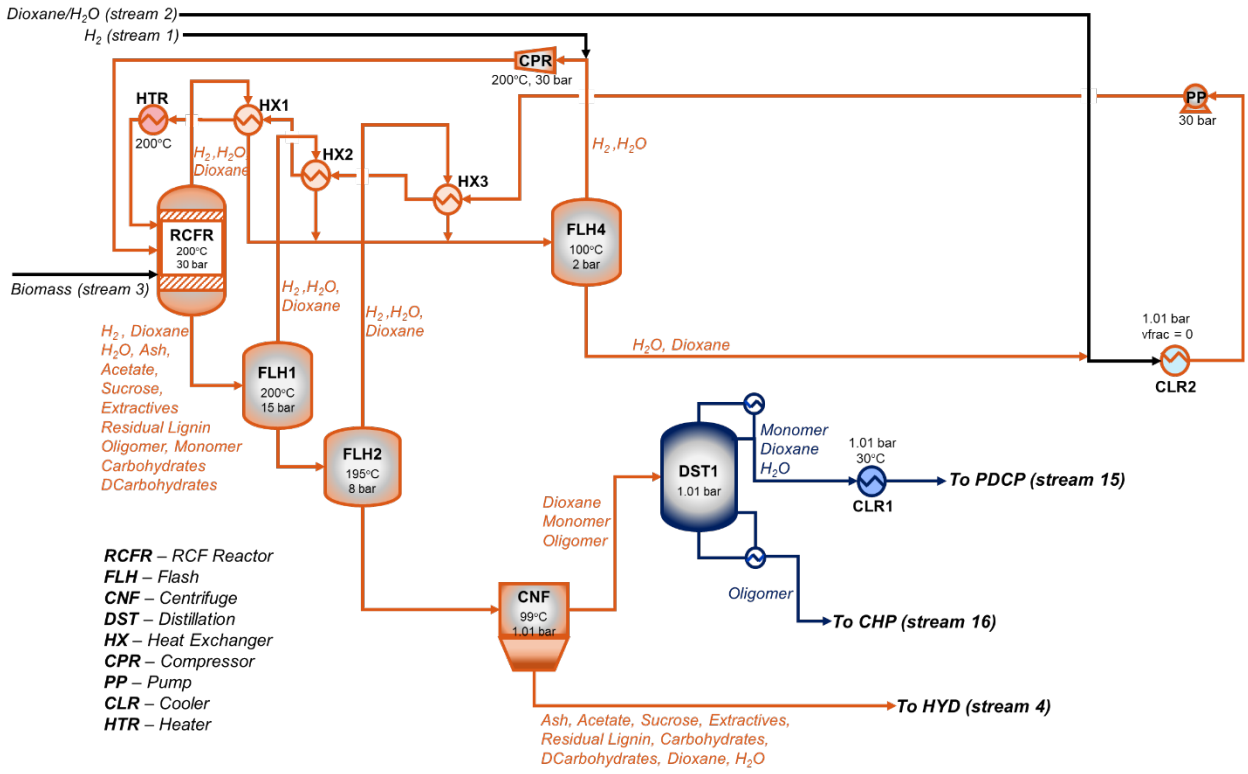

Fig. S23. Process description of RCF and MNP blocks simulated in ASPEN PLUS for the Diox/water system

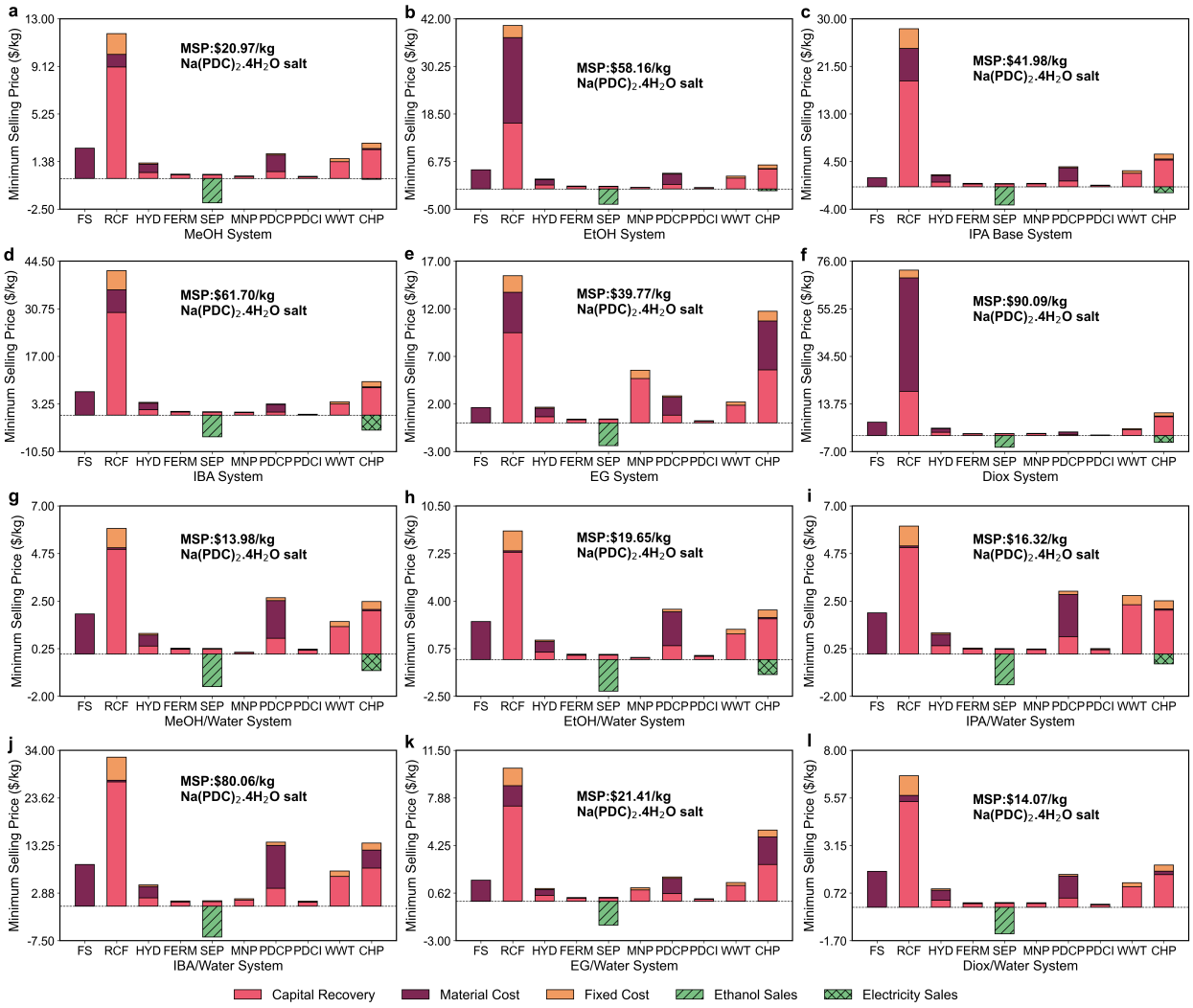

Fig. S24. Breakdown of minimum selling price for each system across each block. Abbreviations: FS: Feedstock, RCF: Reductive Catalytic Fractionation, HYD: Hydrolysis, FERM: Fermentation, SEP: Separation, WWT: Wastewater Treatment, CHP: Combined Heat and Power, MNP: Monomer Purification, PDCP: PDC Production, PDCI: PDC Isolation.

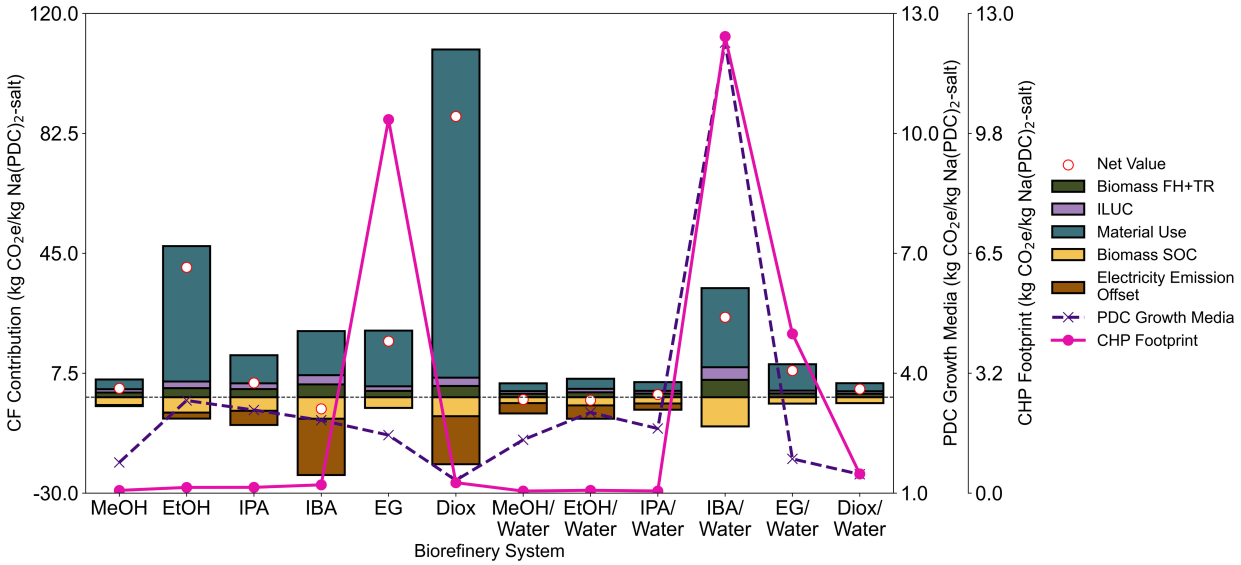

Fig. S25. Carbon footprint (CF) based on economic allocation. Abbreviation: FH: Farm Handling, FT: Transportation, ILUC: Induced Land Use Change, SOC: Soil Organic Carbon sequestration.

Economic and Life Cycle Data

Table S10. List of economic parameters and assumptions

Biomass ($ per metric ton)[a]	115.0
Methanol ($ per metric ton)[a]	362.7
Catalyst (5 wt% Pd/C, $ per kg)[a]	308.3
Hydrogen ($ per metric ton)[a]	1479.6
Glucose ($ per metric ton)[e]	1109.6
Electricity ($ per kWh)[d]	0.0808
Natural Gas ($ per metric ton)[e]	312.7
Cooling Water ($ per metric ton)[j]	0.00030
Fired Heat ($ per MJ)[j]	0.00598
Disposal of ash ($ per metric ton)[g]	48.3
Boiler chemicals ($ per metric ton)[g]	7582.6
FGD lime ($ per metric ton)[g]	302.7
Fresh Water ($ per metric ton)[e]	0.65
Disodium phosphate ($ per ton)[e]	497.5
Monopotassium phosphate ($ per metric ton)[b]	1113.0
Ammonium Sulfate ($ per metric ton)[h]	347.6
NaCl ($ per metric ton)[k]	124.9
Corn steep liquor ($ per metric ton)[f]	103.4
Caustic ($ per metric ton)[g]	210.8
Ethanol ($ per metric ton)[e]	872.3
Isopropanol ($ per metric ton)[b]	981.4
Isobutanol ($ per metric ton)[h]	1631.9
Ethylene Glycol ($ per metric ton)[a]	961.8
1,4-Dioxane ($ per metric ton)[h]	2470.1
Ethanol selling price ($ per GGE)[a]	2.50

All costs are indexed to 2024$, economic assumptions consistent with NREL reports[16-18]

- Internal rate of return (IRR) is assumed to be 30% to reflect the higher risk in investing in new technology[19]
- 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., 2021.[20]
[b]Taken from Alibaba[21]
[d]Taken from EIA[22]
[e]Taken from NREL 2018[16]
[f]Taken from NREL 2011[17]
[g]Taken from NREL 2015[18]
[h]Taken from Intratec[23]
[i]Taken from Liao et al., 2020.[24]
[j]Estimated from Aspen Process Economic Analyzer
[k]Taken from Indywaterpros[25]
[l]Taken from Crux[26]
[m]Taken from EPA[27]
[n]Taken from DOE[28]

Table S11. 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% 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
Ethanol (kg CO_2e per kg) [b]	1.7224
Isopropanol (kg CO_2e per kg) [b]	1.9100
Isobutanol (kg CO_2e per kg) [b]	3.0345
Ethylene glycol (kg CO_2e per kg) [b]	1.9629
1,4-Dioxane (kg CO_2e per kg) [b]	5.3521
Natural Gas as fuel (kg CO_2e per kg) [b]	0.3238

[a]Taken from Gelfand et al., 2020.[29]
[b]Taken from Wang et al., 2023.[30]

Table S12. Allocation for carbon footprint analysis of MeOH System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2195	0.7805	0.9133	0.0867
Biomass (FH + TR)	0.2195	0.7805	0.9133	0.0867
Induced land-use change (ILUC)	0.2195	0.7805	0.9133	0.0867
RCF	0.2195	0.7805	0.9133	0.0867
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2195	0.7805	0.9133	0.0867
CHP (electricity offset included)	0.2195	0.7805	0.9133	0.0867
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S13. Allocation for carbon footprint analysis of EtOH System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.1283	0.8717	0.9386	0.0614
Biomass (FH + TR)	0.1283	0.8717	0.9386	0.0614
Induced land-use change (ILUC)	0.1283	0.8717	0.9386	0.0614
RCF	0.1283	0.8717	0.9386	0.0614
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.1283	0.8717	0.9386	0.0614
CHP (electricity offset included)	0.1283	0.8717	0.9386	0.0614
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S14. Allocation for carbon footprint analysis of IPA System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.1464	0.8536	0.9278	0.0722
Biomass (FH + TR)	0.1464	0.8536	0.9278	0.0722
Induced land-use change (ILUC)	0.1464	0.8536	0.9278	0.0722
RCF	0.1464	0.8536	0.9278	0.0722
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.1464	0.8536	0.9278	0.0722
CHP (electricity offset included)	0.1464	0.8536	0.9278	0.0722
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S15. Allocation for carbon footprint analysis of IBA System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.0820	0.9180	0.9078	0.0922
Biomass (FH + TR)	0.0820	0.9180	0.9078	0.0922
Induced land-use change (ILUC)	0.0820	0.9180	0.9078	0.0922
RCF	0.0820	0.9180	0.9078	0.0922
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.0820	0.9180	0.9078	0.0922
CHP (electricity offset included)	0.0820	0.9180	0.9078	0.0922
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S16. Allocation for carbon footprint analysis of EG System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.1902	0.8098	0.9435	0.0565
Biomass (FH + TR)	0.1902	0.8098	0.9435	0.0565
Induced land-use change (ILUC)	0.1902	0.8098	0.9435	0.0565
RCF	0.1902	0.8098	0.9435	0.0565
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.1902	0.8098	0.9435	0.0565
CHP (electricity offset included)	0.1902	0.8098	0.9435	0.0565
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S17. Allocation for carbon footprint analysis of Diox System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.0979	0.9021	0.9458	0.0542
Biomass (FH + TR)	0.0979	0.9021	0.9458	0.0542
Induced land-use change (ILUC)	0.0979	0.9021	0.9458	0.0542
RCF	0.0979	0.9021	0.9458	0.0542
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.0979	0.9021	0.9458	0.0542
CHP (electricity offset included)	0.0979	0.9021	0.9458	0.0542
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S18. Allocation for carbon footprint analysis of MeOH/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2664	0.7336	0.9007	0.0993
Biomass (FH + TR)	0.2664	0.7336	0.9007	0.0993
Induced land-use change (ILUC)	0.2664	0.7336	0.9007	0.0993
RCF	0.2664	0.7336	0.9007	0.0993
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2664	0.7336	0.9007	0.0993
CHP (electricity offset included)	0.2664	0.7336	0.9007	0.0993
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S19. Allocation for carbon footprint analysis of EtOH/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2067	0.7933	0.9219	0.0781
Biomass (FH + TR)	0.2067	0.7933	0.9219	0.0781
Induced land-use change (ILUC)	0.2067	0.7933	0.9219	0.0781
RCF	0.2067	0.7933	0.9219	0.0781
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2067	0.7933	0.9219	0.0781
CHP (electricity offset included)	0.2067	0.7933	0.9219	0.0781
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S20. Allocation for carbon footprint analysis of IPA/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2777	0.7223	0.9181	0.0819
Biomass (FH + TR)	0.2777	0.7223	0.9181	0.0819
Induced land-use change (ILUC)	0.2777	0.7223	0.9181	0.0819
RCF	0.2777	0.7223	0.9181	0.0819
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2777	0.7223	0.9181	0.0819
CHP (electricity offset included)	0.2777	0.7223	0.9181	0.0819
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S21. Allocation for carbon footprint analysis of IBA/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.0772	0.9228	0.9228	0.0772
Biomass (FH + TR)	0.0772	0.9228	0.9228	0.0772
Induced land-use change (ILUC)	0.0772	0.9228	0.9228	0.0772
RCF	0.0772	0.9228	0.9228	0.0772
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.0772	0.9228	0.9228	0.0772
CHP (electricity offset included)	0.0772	0.9228	0.9228	0.0772
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S22. Allocation for carbon footprint analysis of EG/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2359	0.7641	0.9219	0.0781
Biomass (FH + TR)	0.2359	0.7641	0.9219	0.0781
Induced land-use change (ILUC)	0.2359	0.7641	0.9219	0.0781
RCF	0.2359	0.7641	0.9219	0.0781
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2359	0.7641	0.9219	0.0781
CHP (electricity offset included)	0.2359	0.7641	0.9219	0.0781
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Table S23. Allocation for carbon footprint analysis of Diox/water System. Economic allocation is calculated using biofuel (ethanol selling price) and calculated MSP of $Na(PDC)_2$-salt

Category	Mass allocation		Economic Allocation	
	$Na(PDC)_2$-salt	Biofuel	$Na(PDC)_2$-salt	Biofuel
Biomass (SOC)	0.2936	0.7064	0.9126	0.0874
Biomass (FH + TR)	0.2936	0.7064	0.9126	0.0874
Induced land-use change (ILUC)	0.2936	0.7064	0.9126	0.0874
RCF	0.2936	0.7064	0.9126	0.0874
HYD	0.0000	1.0000	0.0000	1.0000
FERM	0.0000	1.0000	0.0000	1.0000
SEP	0.0000	1.0000	0.0000	1.0000
WWT	0.2936	0.7064	0.9126	0.0874
CHP (electricity offset included)	0.2936	0.7064	0.9126	0.0874
MNP	1.0000	0.0000	1.0000	0.0000
PDCP	1.0000	0.0000	1.0000	0.0000
PDCI	1.0000	0.0000	1.0000	0.0000

Leave-one-solvent-out cross-validation of the quadratic regression model

To demonstrate the predictive power of the quadratic regression model developed in this work for new solvents, we performed leave-one-solvent-out cross-validation. In this approach, each solvent (and its aqueous mixtures) was iteratively designated as the test set, while the parameters of the quadratic regression with interaction terms model (as described in Eqn. 4 of the main text) were fitted using the remaining five solvents as the training set. Table S24 reports R^2 and RMSE values for both the training set and test set predictions. These results show that leaving out any solvent other than EG leads to good prediction performance for the left-out solvent; leaving out EG leads to weak predictions, but since this solvent (and its mixtures) lead to the largest δ_H values we attribute these poor predictions to the need for model extrapolation. An example parity plot while using ethanol (and its aqueous mixtures) as test set is shown in Fig.S26, with an R^2 value of 0.85 and RMSE value of 0.53. These results demonstrate the robustness and predictive accuracy of the quadratic regression model.

Table S24. Leave-one-out validation of quadratic regression with interaction terms model for RCF monomer yield (wt% biomass).

Test set solvent/mixtures	Training set		Test set	
	R^2	$RMSE$	R^2	RMSE
EG	0.93	0.55	-1.20	0.71
MeOH	0.91	0.58	0.98	0.52
EtOH	0.93	0.56	0.85	0.53
IPA	0.93	0.49	0.86	0.86
IBA	0.92	0.51	0.89	0.77
Diox	0.89	0.59	0.82	0.57
*	0.92	0.55	-	-

*All solvents are part of the training set.

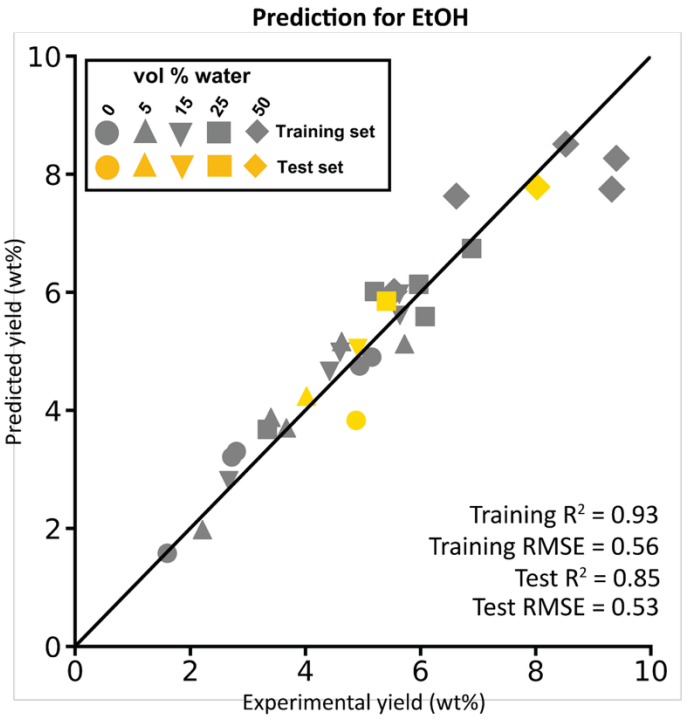

Fig. S26. Prediction of RCF monomer yield (wt% biomass) using EtOH as test set with all other solvent systems considering as training set. The R^2 and RMSE values for both the training and test sets are shown in the bottom right corner. A summary of the R^2 and RMSE values for other solvents used as test sets is provided in Table S24.

Table S25. Leave-one-out validation of quadratic regression with interaction terms model for PDC yield (wt% biomass).

Test set solvent/mixtures	Training set		Test set	
	R^2	$RMSE$	R^2	RMSE
EG	0.93	0.33	0.73	0.40
MeOH	0.92	0.33	0.84	0.31
EtOH	0.96	0.26	0.55	0.53
IPA	0.92	0.32	0.94	0.33
Diox	0.86	0.33	0.77	0.67
*	0.92	0.32	-	-

*All solvents are part of the training set.

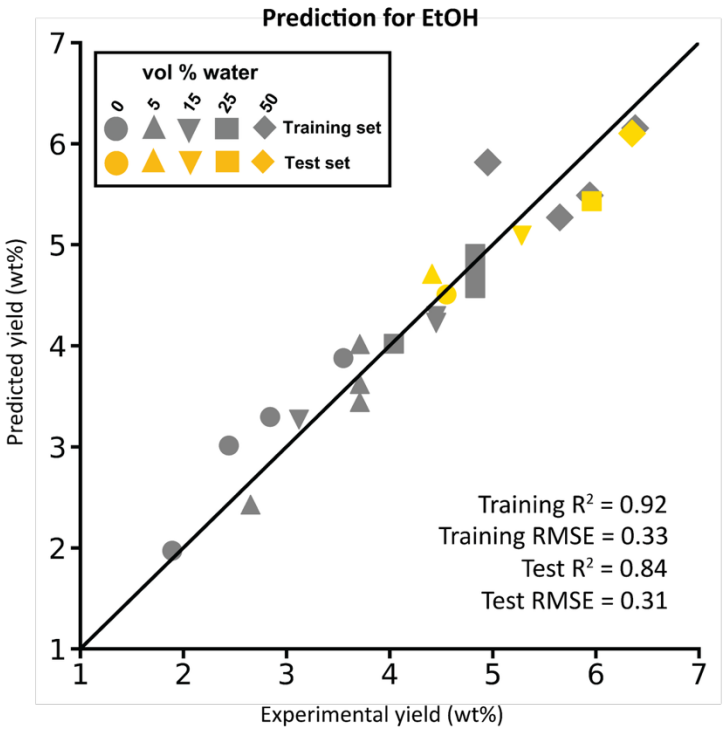

Fig. S27. Prediction of PDC yield (wt% biomass) using EtOH as test set with all other solvent systems considering as training set. The R^2 and RMSE values for both the training and test sets are shown in the bottom right corner. A summary of the R^2 and RMSE values for other solvents used as test sets is provided in Table S25.

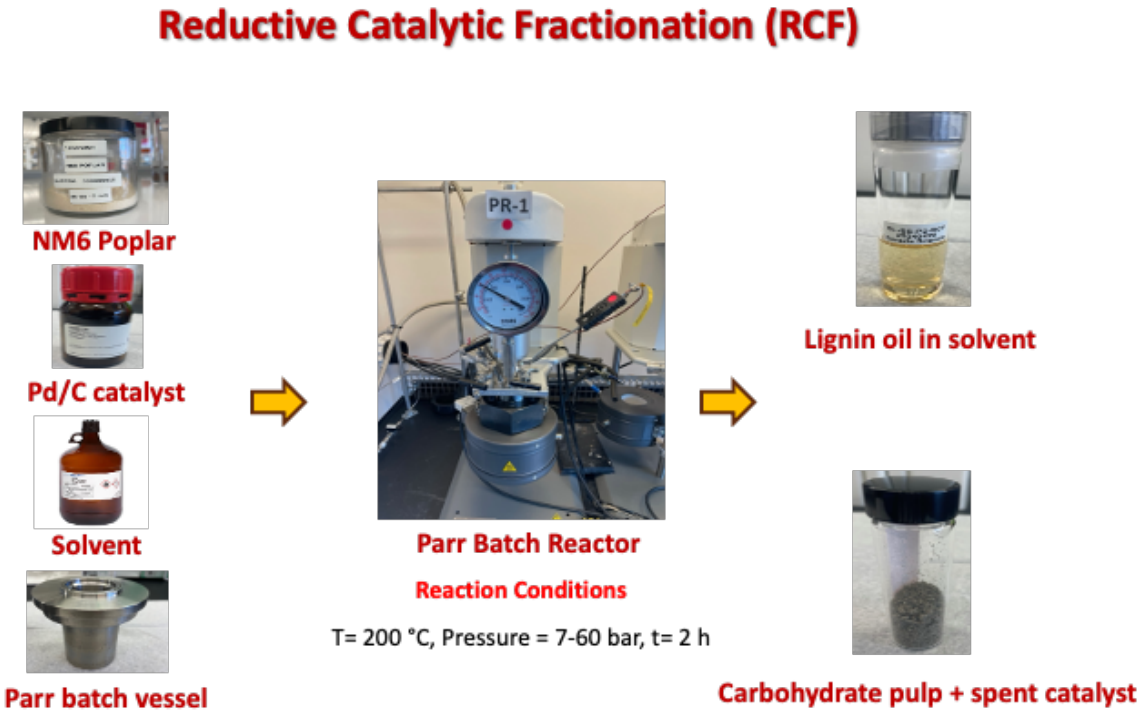

Fig. S28 Scheme depicting the experimental procedure for RCF reactions with NM6 poplar producing lignin oil in solvent and a solid fraction (carbohydrate pulp and spent catalyst).

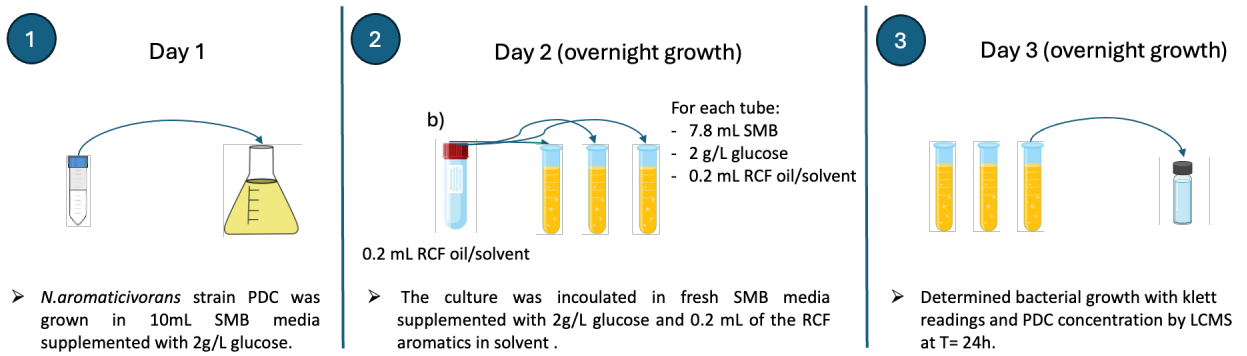

Fig. S29. Scheme depicting the experimental procedure for microbial PDC production with *N.aromaticivorans.*

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