Supplemental Information: Energy and techno-economic analysis of bio-based carboxylic acid recovery by adsorption

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Table S1. Adsorption studies for carboxylic acid recovery

Reference	Resin name	Resin functionality	Acid(s) studied	Elution method
Srivastava *et al.* (1992)[1]	Amberlite IRA-400	Quaternary amine	Lactic acid	2.5 M HCl
Fu *et al.* (2002)[2]	Amberlite IRA-400	Quaternary amine	Fumaric acid	n/a
Cao *et al.* (2002)[3]	Amberlite IRA-400	Quaternary amine	Lactic acid	1.0 M H_2SO_4
Sosa *et al.* (2001)[4]	Amberlite IRA-400	Quaternary amine	Lactic acid	4 M HCl
González-Vara *et al.* (2000)[5]	Amberlite IRA-420	Strong anion exchanger	Lactic acid	5% ammonium carbonate
Magalhães Jr. *et al.* (2015)[6]	A-500P, PFA-300	Strong anion exchanger	Itaconic acid	2 M HCl
Monteagudo & Aldavero (1999)[7]	Amberlite IRA-420	Strong anion exchange	Lactic acid	Ammonium carbonate
Leite *et al.* (2008)[8]	Dowex Marathon A	Quaternary amine	Acetic, propionic, butyric acid	pH 12 NaOH
Cao *et al.* (1996)[9]	Amberlite IRA-900	Quaternary amine	Fumaric acid	0.4 M NaCl
Zhang & Yang (2015)[10]	Amberlite IRA-900	Quaternary amine	Fumaric acid	0.7 M NaCl, 0.7 M NaOH
López-Garzón *et al.* (2015)[11]	Dowex marathon MSA	Quaternary amine	2,5-furandicarboxylic acid, succinic acid	Reaction with dimethyl carbonate
López-Garzón *et al.* (2012)[12]	Dowex marathon MSA	Quaternary amine	Succinic acid	Reaction with chloroethane
Dethe *et al.* (2006)[13]	Indion 850	Quaternary and tertiary amine	Lactic acid	n/a
Bayazit *et al.* (2009)[14]	Amberlite IRA-67	Tertiary amine	Glutaric acid, glyoxylic acid	n/a
Garcia & King (1989)[15]	Dowex MWA-1	Tertiary amine	Acetic acid	Methanol
Dai & King (1996)[16]	Dowex MWA-1, Amberlite IRA-35	Tertiary amine	Lactic acid	n/a
Husson & King (1998)[17]	Dowex MWA-1, Amberlite IRA-35	Tertiary amine	Lactic acid, succinic acid	10 wt % trimethylamine in methyl isobutyl ketone
Gao *et al.* (2010)[18]	IRA-67	Tertiary amine	Lactic acid	4 wt % NaOH
Jun *et al.* (2007)[19]	mesoporous silica SBA-15	Primary, secondary and tertiary amine	pyruvic acid, succinic acid	n/a
Kawabata *et al.* (1981)[20]	IRA-400	Primary, secondary and tertiary amine	n/a	Methanol, acetone, 2-propanol
Chen & Ju (2002)[21]	Polyvinylpyridine (PVP)	Pyridine	Lactic acid	0.1 M NaOH
Kawabata *et al.* (1981)[20]	Polyvinylpyridine (PVP)	Pyridine	Formic, acetic, propionic, butyric, valeric, acrylic,	Methanol, acetone, 2-propanol

			methacrylic, lactic, glycolic, adipic, malic, maleic, citric acid	
Chanda et al. (1985)[22]	Polyvinylpyridine (PVP)	Pyridine	Formic, acetic, propionic, butyric acid	0.1 M NaOH
Van den Bergh et al. (2017)[23]	Polyvinylpyridine (PVP)	Pyridine	Citric acid	Acetone, propanol, acetonitrile, ethanol, methanol
Garcia & King (1989)[15]	Polyvinylpyridine (PVP)	Pyridine	Acetic acid	Methanol
Dai & King (1996)[16]	Reillex 425	Pyridine	Lactic acid	n/a
Husson & King (1998)[17]	Reillex 425	Pyridine	Lactic acid, succinic acid	10 wt % trimethylamine in methyl isobutyl ketone
Wu et al. (2009)[24]	Polyvinylpyridine (PVP)	Pyridine	Citric acid	90°C water
Delgado et al. (2018)[25]	Polyvinylpyridine (PVP)	Pyridine	Lactic acid	Methanol
Chanda et al. (1985)[22]	Polybenzimidazole (PBI)	benzimidazole	Formic, acetic, propionic, butyric acid	0.1 M NaOH
Garcia & King (1989)[15]	Polybenzimidazole (PBI)	benzimidazole	Acetic acid	Methanol
Chen & Ju (2002)[21]	Activated carbon	n/a	Lactic acid	0.1 M NaOH
Gao et al. (2010)[18]	Activated carbon	n/a	Lactic acid	4 wt % NaOH
Efe et al. (2010)[26]	CVB28014 (high-silica ZSM-5)	n/a	Succinic acid	n/a

Table S2. Composition of Cyanex 923[27]

Component	wt%
trihexylphosphine oxide	8.5
octyldihexylphosphine oxide	30.4
dioctylhexylphosphine oxide	37.4
trioctylphosphine oxide	16.1
branched alkyl groups	7.3

Table S3. β-values for Common Solvents

Solvent	$\Delta\tilde{v}(OH - OMe)$	$\beta(OH)$
water	910	0.448
acetone	1010	0.498
methanol	1440	0.709
dimethyl sulfoxide	1500	0.739

triethylamine	2320	1.143

Kamlet and Taft developed a solvatochromic scale for determining a solvent's hydrogen bond acceptor strength by measuring the hydrogen bond shifts of two reference probes, 4-nitrophenol and 4-nitroaniline, in the solvent of interest.[28] The two reference probes are identical except in that the hydroxyl group in 4-nitrophenol is replaced with a non-hydrogen bonding methoxy group in 4-nitroaniline. By subtracting the hydrogen bond shift of 4-nitroaniline $(\Delta\tilde{v}(OMe))$ from that of 4-nitrophenol $(\Delta\tilde{v}(OH))$, one can determine the $\Delta\tilde{v}$ shift that is attributable solely to hydrogen bonding $(\Delta\tilde{v}(OH-OMe))$, and not to other intermolecular forces, such as Van der Waals'. The $\Delta\tilde{v}(OMe)$ values can then be scaled to a range of 0-1 by normalizing to the $\Delta\tilde{v}(OH-OMe)$ of hexamethylphosphoric triamide (HMPA) as seen in the equation S1 below:

$$\beta(OH) = \frac{\Delta\tilde{v}(OH-OMe)}{2030} \qquad S1$$

The $\Delta\tilde{v}(OH-OMe)$ values for the solvents used in this work were taken from tables in Gal and Laurence's *Lewis Basicity and Affinity Scales*.[29] The $\beta(OH)$ values were then calculated using equation S1 above. The $\beta(OH)$ value for triethylamine was used as the estimated value for Cyanex 923 because the $\beta(OH)$ for tri-hexyl and tri-octyl phosphine oxides are not known and triethylamine has similar donor number (an alternative basicity scale) as tri-octyl phosphine oxide.

Table S4. Stream Table for 90.57 g per L Butyric Acid with Acetone and 5 wt% Water

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9
Temperature (°C)	20.0	20.0	20.0	20.7	27.1	82.7	63.8	58.0	20.8
Pressure (atm)	0.16	0.16	0.16	0.16	0.10	0.10	0.25	0.25	0.25
Total Mass Flow (kg/hr)	8.980	6.088	2.892	2.892	1.912	0.980	8.000	8.000	7.355
Mass Fraction Butyric Acid	0.111	0.002	0.342	0.342	0.010	0.991	0.004	0.004	0.000
Mass Fraction Acetone	0.839	0.968	0.566	0.566	0.856	0.001	0.941	0.941	0.991
Mass Fraction Water	0.050	0.031	0.091	0.091	0.134	0.008	0.055	0.055	0.009

	Stream 9	Stream 10	Stream 11	Stream 12	Stream 13	Stream 14	Stream 15	Stream 16	Stream 17
Temperature (°C)	20.8	31.4	20.9	31.4	31.4	48.0	31.4	30.7	30.8
Pressure (atm)	0.25	0.25	1.00	0.25	0.25	0.25	1.00	0.10	1.00
Total Mass Flow (kg/hr)	7.355	0.807	7.355	0.645	0.161	0.161	0.645	0.980	0.980

Mass Fraction Butyric Acid	0.000	0.045	0.000	0.045	0.045	0.045	0.045	0.991	0.991
Mass Fraction Acetone	0.991	0.370	0.991	0.370	0.370	0.370	0.370	0.001	0.001
Mass Fraction Water	0.009	0.585	0.009	0.585	0.585	0.585	0.585	0.008	0.008

Table S5. Stream Table for 90.57 g per L Butyric Acid with 10 wt% TOA-acetone and 5 wt.% Water

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9
Temperature (°C)	20.0	20.0	20.0	31.4	79.6	268.9	67.3	20.7	73.2
Pressure (atm)	0.10	0.10	0.10	0.10	0.10	0.10	0.06	0.06	0.06
Total Mass Flow (kg/hr)	8.972	6.406	2.566	2.566	1.796	0.769	1.796	0.829	0.968
Mass Fraction Butyric Acid	0.111	0.005	0.378	0.378	0.540	0.000	0.540	0.014	0.990
Mass Fraction TOA	0.086	0.000	0.300	0.300	0.000	1.000	0.000	0.000	0.000
Mass Fraction Acetone	0.747	0.941	0.262	0.262	0.374	0.000	0.374	0.802	0.007
Mass Fraction Water	0.056	0.054	0.060	0.060	0.086	0.000	0.086	0.183	0.003

	Stream 10	Stream 11	Stream 12	Stream 13	Stream 14	Stream 15	Stream 16	Stream 17	Stream 18
Temperature (°C)	91.3	85.0	20.7	32.1	32.1	32.1	75.0	20.8	32.2
Pressure (atm)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.00	1.00
Total Mass Flow (kg/hr)	7.235	7.235	6.475	0.800	0.040	0.760	0.040	6.475	0.760
Mass Fraction Butyric Acid	0.006	0.006	0.000	0.055	0.055	0.055	0.055	0.000	0.055

Mass Fraction TOA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mass Fraction Acetone	0.926	0.926	0.993	0.348	0.348	0.348	0.348	0.993	0.348
Mass Fraction Water	0.069	0.069	0.007	0.598	0.598	0.598	0.598	0.007	0.598

	Stream 17	Stream 18	Stream 19	Stream 20	Stream 21
Temperature (°C)	20.8	32.2	73.4	41.4	41.5
Pressure (atm)	1.00	1.00	1.00	0.10	1.00
Total Mass Flow (kg/hr)	6.475	0.760	0.968	0.769	0.769
Mass Fraction Butyric Acid	0.000	0.055	0.990	0.000	0.000
Mass Fraction TOA	0.000	0.000	0.000	1.000	1.000
Mass Fraction Acetone	0.993	0.348	0.007	0.000	0.000
Mass Fraction Water	0.007	0.598	0.003	0.000	0.000

Table S6. Stream Table for 90.57 g per L Butyric Acid with Methanol and 5 wt.% Water

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9
Temperature (°C)	25.0	21.8	24.4	24.4	24.4	54.1	24.7	82.5	52.2
Pressure (atm)	0.12	0.12	0.12	0.12	0.12	0.12	0.1	0.1	0.15
Total Mass Flow (kg/hr)	8.990	5.733	3.290	3.257	0.033	0.033	2.259	0.998	7.992
Mass Fraction Butyric Acid	0.111	0.000	0.306	0.306	0.306	0.306	0.004	0.991	0.001
Mass Fraction Methanol	0.839	0.967	0.614	0.614	0.614	0.614	0.882	0.006	0.943
Mass Fraction Water	0.050	0.033	0.080	0.080	0.080	0.080	0.114	0.004	0.056

	Stream 10	Stream 11	Stream 12	Stream 13	Stream 14	Stream 15	Stream 16	Stream 17
Temperature (°C)	21.0	19.9	41.6	19.9	41.6	64.1	64.2	21.0
Pressure (atm)	0.13	0.13	0.13	1.00	1.00	0.10	1.00	0.13
Total Mass Flow (kg/hr)	7.992	7.550	0.442	7.550	0.442	0.998	0.998	7.992
Mass Fraction Butyric Acid	0.001	0.000	0.026	0.000	0.026	0.991	0.991	0.001

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Mass Fraction Methanol	0.943	0.991	0.123	0.991	0.123	0.006	0.006	0.943
Mass Fraction Water	0.056	0.009	0.851	0.009	0.851	0.004	0.004	0.056

Table S7. Separation cost associated with capital expenditures

Resin			PVP			
Solvent			Water	Acetone	Cyanex/Acetone (10:90)	Methanol
Total Installed Cost (TIC)			$ 23,041,532	$ 18,407,532	$ 18,935,532	$ 17,723,532
Warehouse	4.0%	of TIC	$ 921,661	$ 736,301	$ 757,421	$ 708,941
Site Development	9.0%	of TIC	$ 2,073,738	$ 1,656,678	$ 1,704,198	$ 1,595,118
Additional Piping	4.5%	of TIC	$ 1,036,869	$ 828,339	852,099	797,559
Total Direct Costs (TDC)			$ 27,073,800	$ 21,628,850	$ 22,249,250	$ 20,825,150
Prorateable Expenses	10.0%	of TDC	$ 2,707,380	$ 2,162,885	$ 2,224,925	$ 2,082,515
Field Expenses	10.0%	of TDC	$ 2,707,380	$ 2,162,885	$ 2,224,925	$ 2,082,515
Home Office & Construction Fee	20.0%	of TDC	$ 5,414,760	$ 4,325,770	$ 4,449,850	$ 4,165,030
Project Contingency	10.0%	of TDC	$ 2,707,380	$ 2,162,885	$ 2,224,925	$ 2,082,515
Other Costs (Start-Up, Permits, etc.)	10.0%	of TDC	$ 2,707,380	$ 2,162,885	$ 2,224,925	$ 2,082,515
Total Indirect Costs			$ 16,244,280	$ 12,977,310	$ 13,349,550	$ 12,495,090
Fixed Capital Investment (FCI)			$ 43,318,081	$ 34,606,161	$ 35,598,801	$ 33,320,241
Plant Life	30	years				
Capital Depreciation			$ 2,165,904	$ 1,730,308	$ 1,779,940	$ 1,666,012
Butyric Acid Yield	21,075	kg/hr				
Operating Hours per Annum	7,884	hr				
Separation Cost ($/kg butyric acid)			0.01	0.01	0.01	0.01

Resin			Dowex 77				Strong Ion
Solvent			Water	Acetone	Cyanex/Acetone (10:90)	Methanol	4M HCl
Total Installed Cost (TIC)			$ 23,041,532	$ 19,619,532	$ 20,493,532	$ 19,632,532	$ 7,347,532
Warehouse			$ 921,661	$ 784,781	$ 819,741	$ 785,301	$ 293,901
Site Development			$ 2,073,738	$ 1,765,758	$ 1,844,418	$ 1,766,928	$ 661,278

Additional Piping	$ 1,036,869	$ 882,879	$ 922,209	$ 883,464	$ 330,639
Total Direct Costs (TDC)	**$ 27,073,800**	**$ 23,052,950**	**$ 24,079,900**	**$ 23,068,225**	**$ 8,633,350**
Prorateable Expenses	$ 2,707,380	$ 2,305,295	$ 2,407,990	$ 2,306,823	$ 863,335
Field Expenses	$ 2,707,380	$ 2,305,295	$ 2,407,990	$ 2,306,823	$ 863,335
Home Office & Construction Fee	$ 5,414,760	$ 4,610,590	$ 4,815,980	$ 4,613,645	$ 1,726,670
Project Contingency	$ 2,707,380	$ 2,305,295	$ 2,407,990	$ 2,306,823	$ 863,335
Other Costs (Start-Up, Permits, etc.)	$ 2,707,380	$ 2,305,295	$ 2,407,990	$ 2,306,823	$ 863,335
Total Indirect Costs	**$ 16,244,280**	**$ 13,831,770**	**$ 14,447,940**	**$ 13,840,935**	**$ 5,180,010**
Fixed Capital Investment (FCI)	**$ 43,318,081**	**$ 36,884,721**	**$ 38,527,841**	**$ 36,909,161**	**$ 13,813,361**
Capital Depreciation	**$ 2,165,904**	**$ 1,844,236**	**$ 1,926,392**	**$ 1,845,458**	**$ 690,668**
Separation Cost ($/kg butyric acid)	**0.01**	**0.01**	**0.01**	**0.01**	**0.004**

Table S8. OPEX costs associated with raw materials and utilities

	Unit Price	Unit	Source
Resin costs			
PVP	875	$/kg	Vertellus[1]
Dowex 77	15	$/kg	Lenntech
Solvent costs			
Acetone	0.78	$/L	IHS Markit – PEP[3]
Methanol	0.27	$/L	IHS Markit – PEP[3]
Water	0.00038	$/L	
Cyanex 923	20	$/L	Solvay[5]
NaOH (50 wt.%)	0.41	$/kg	IHS - PEP
HCl (35.2 wt.%)	0.18	$/kg	IHS – CEH[4]
Low pressure steam (LPS)	5.69	$/GJ	This study
	0.006	$/MJ	
Electricity	0.068	$/kWh	Davis 2018
	0.02	$/MJ	

1. PVP bulk cost was estimated from a 1,500 kg batch
2. Dowex 77 bulk cost was estimated from communication with Lenntech (USA)
3. PEP: Process Economics Program
4. CEH: Chemical Economics Handbooks
5. The Cyanex 923 cost was discounted 40% to account for R&D and scale-up within the field

Table S9. GHG emission and fossil energy demand factors

	GHG	Unit	Fossil Energy	Unit	Reference

PVP	3.39	kg CO2e/kg		57.1	MJ/kg	This study
Dowex 77	3.18	kg CO2e/kg		92.5	MJ/kg	This study
Acetone	1.36	kg CO2e/kg		46.2	MJ/kg	Datasmart
Cyanex 923	15.4	kg CO2e/kg		229	MJ/kg	This study
NaOH (50 wt.%)	1.61	kg CO2e/kg		18.7	MJ/kg	Datasmart
HCl (35.2 wt.%)	0.67	kg CO2e/kg		8.31	MJ/kg	Datasmart
Low pressure steam	0.10	kg CO2e/MJ		0.16	MJ/MJ	GREET
Electricity	0.55	kg CO2e/kWh		6.53	MJ/kWh	GREET

Langmuir equilibrium Isotherm

The Langmuir equilibrium isotherm model which assumes ideal 1:1 molar interaction between adsorbent and active site leads to an uptake plateau (equation S1).

$$q = \frac{q_{max}\, K\, C_{EQ}}{(1 + K\, C_{EQ})}$$

(equation S1)

In equation S1, q and q_{max} are the uptake of acid onto the resin and maximum uptake respectively (g acid per g dry resin), C_{EQ} is the equilibrium concentration of acid in the solution (g L^{-1}), K is the adsorption capacity of the resin (L g^{-1}).

Equations to estimate the Freundlich isotherm parameters (K and n) and the free acid concentration

There is a linear correlation between the logarithm of the adsorption capacity and both the pK$_a$ of the resins' functional group monomer (equation S2) and the apparent pK$_a$ of the resin (equation S3). Equation S4 gives the relationship between the n parameter and the apparent pKa of the resin

$$log_{10}(K) = 0.42\,(pK_a) - 5.1 \qquad (R2 = 0.97) \quad (Equation\ 2)$$

$$log_{10}(K) = 0.6\,(pK_a) - 5.9 \qquad (R2 = 0.99) \quad (Equation\ 3)$$

$$(n) = -0.08\,(pK_a) + 0.97 \qquad (R2 = 0.97) \quad (Equation\ S4)$$

$$(n) = -0.11\,(pK_a) + 1.1 \qquad (R2 = 0.99) \quad (Equation\ S5)$$

$$pH = pK_a + log_{10}\left(\frac{A^-}{HA}\right) \qquad (Equation\ S6)$$

$$Titer = HA + A^- \qquad (equation\ S7)$$
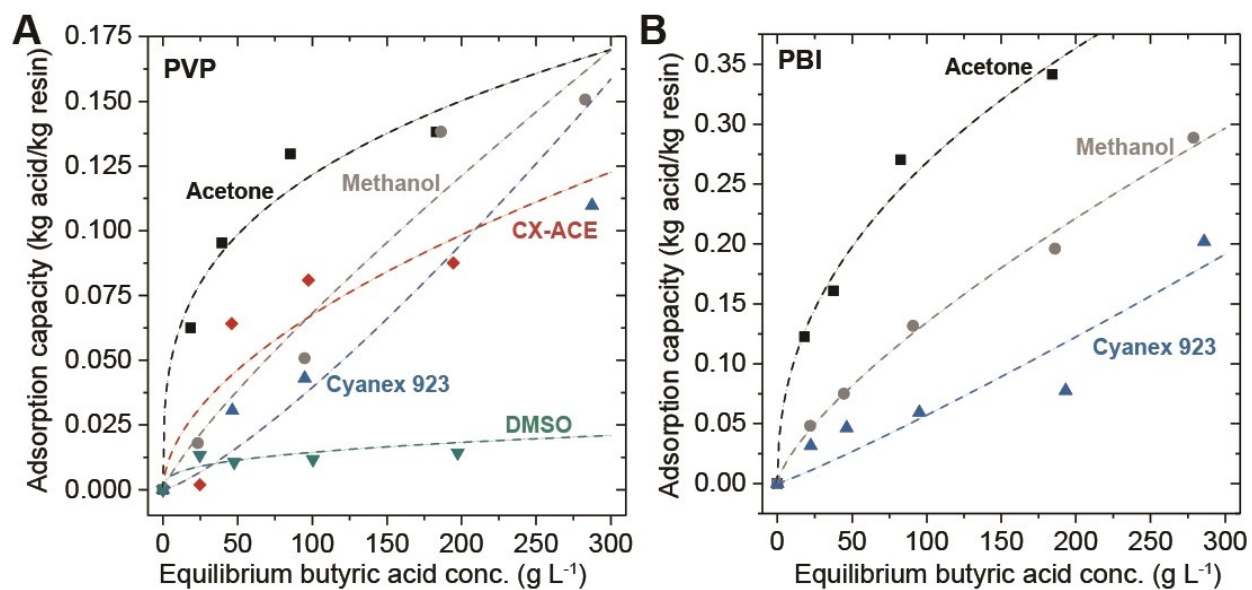
Figure S1. Adsorption Isotherm of Butyric acid
The experimental equilibrium data shows the adsorption of butyric acid onto (A) PVP and (B) PBI resin in the presence of solvents. The data is fit to the Freundlich model (equation 3) to determine the desorption constant of solvents which is a constant that is proportional to the affinity of the acid for the resin.
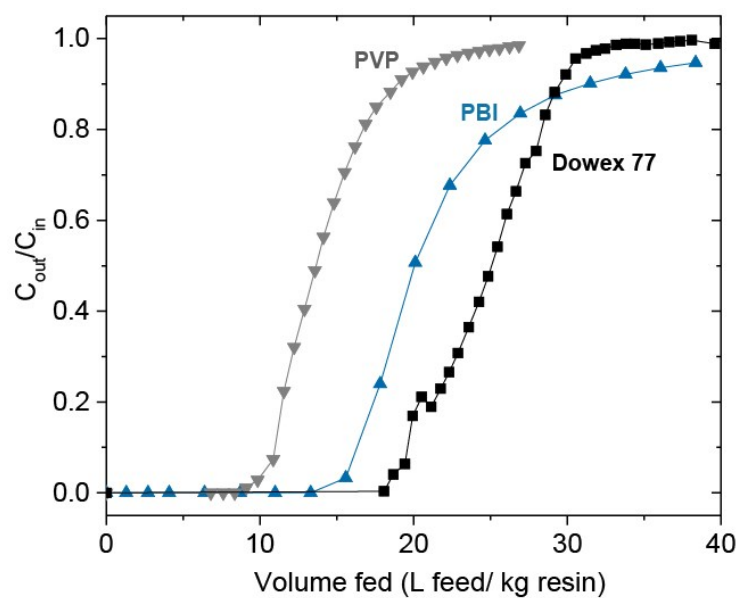
Figure S2. Breakthrough Point (BTP) Curve
The breakthrough point (BTP) of PVP, PBI, and Dowex 77 was determined by flowing a solution of 20 g L^{-1} (C_{in}) butyric acid onto fixed-bed columns. The outlet concentration (C_{out}) of butyric acid was measured to determine the BTP, which corresponds to the volume at which butyric acid begins to be present in the eluate. The BTP was determined to be 7.4 L kg^{-1} resin, 15.5 L kg^{-1} resin, and 18.0 L kg^{-1} for PVP, PBI, Dowex 77 respectively.
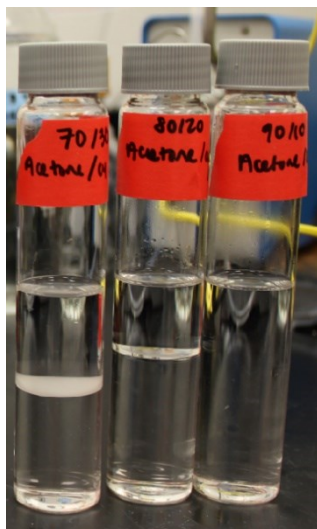
Figure S3. From left to right: 70 wt. % acetone, 30 wt. % Cyanex 923 mixed with water, 80 wt. % acetone, 20 wt. % Cyanex 923 mixed with water, and 90 wt. % acetone, 10 wt. % Cyanex 923 mixed with water. Only the 90 wt. % acetone, 10 wt. % Cyanex 923 is miscible with water and therefore was selected as an elution solvent for fixed-bed experiments.
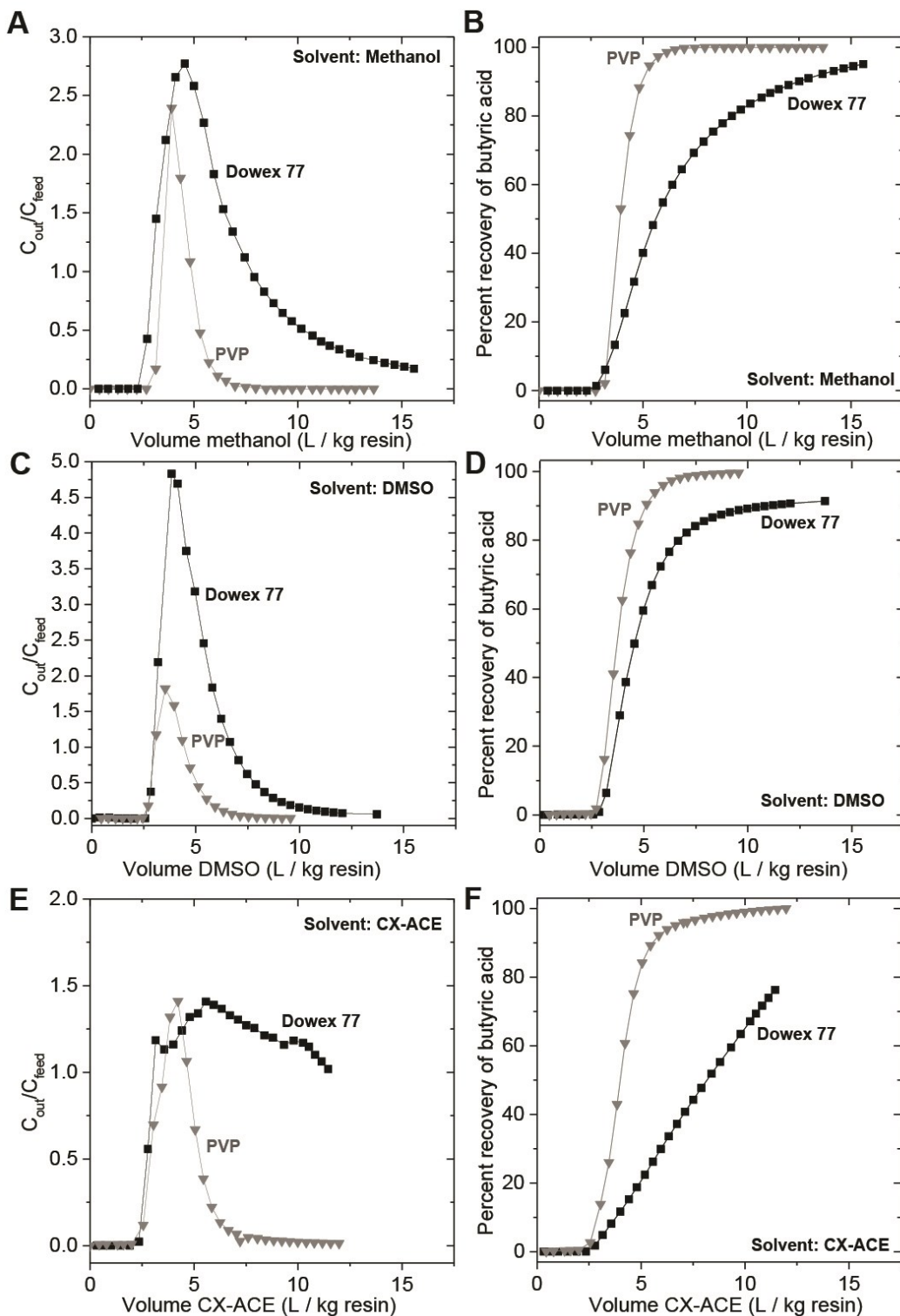
Figure S4. Elution curves Figure S2.
Normalized eluate concentration (C_{out}) for PVP and Dowex 77 using (A) methanol, (C) DMSO, or (E) CX-ACE as the elution solvent. (B) Mass recovery of butyric acid in the eluate as a function of the total (B) methanol, (D) DMSO, or (F) CX-ACE volume used. Surprisingly, the CX-acetone solvent showed poor performance for butyric acid elution as indicated by the tailing on the butyric acid peak in Figure S4E.
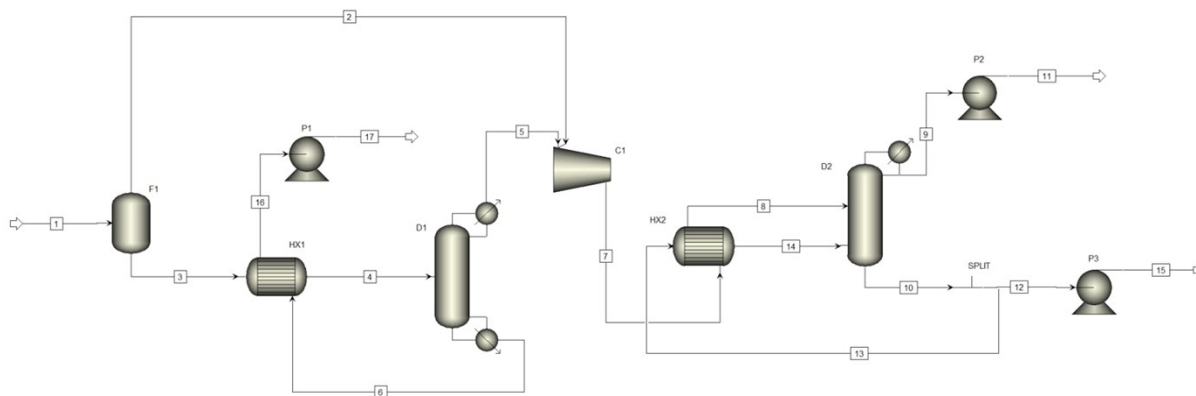
Figure S5. PFD for acetone and methanol recycling and butyric acid isolation. In order to separate the majority of the solvent upfront, a 3 stage RADFRAC distillation was utilized in place of the flash seen in the figure above for the methanol recovery process.
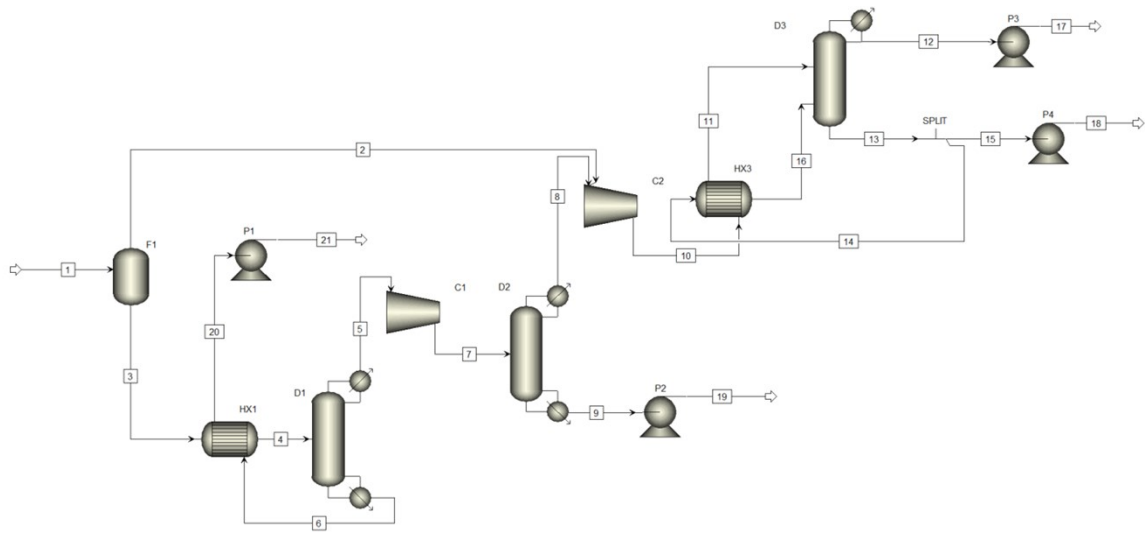
Figure S6. PFD for acetone and TOA or Cyanex 923 recycling and butyric acid isolation
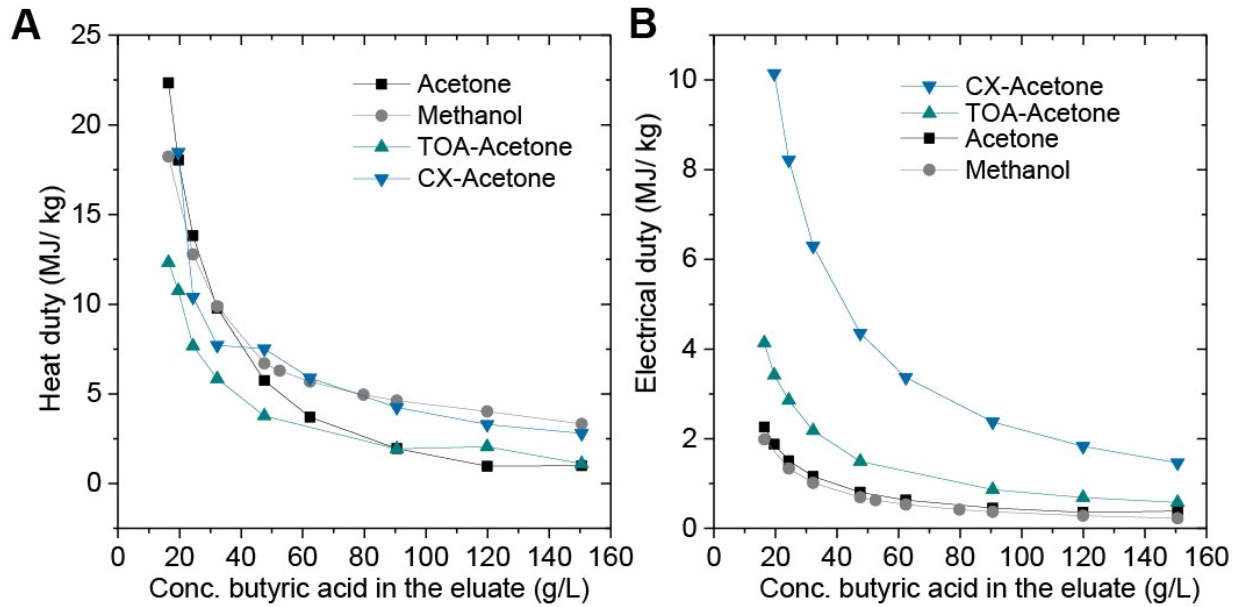
Figure S7. Distillation Heat and Electrical Duty
Distillation heat and electrical duties as a function of butyric acid concentration in the eluate which is the distillation feed stream. The solvent is either methanol, acetone, or 10 wt.% TOA or Cyanex 923 (CX) in acetone. For the CX case, the heating and electric demand was estimated from the TOA-acetone curves.
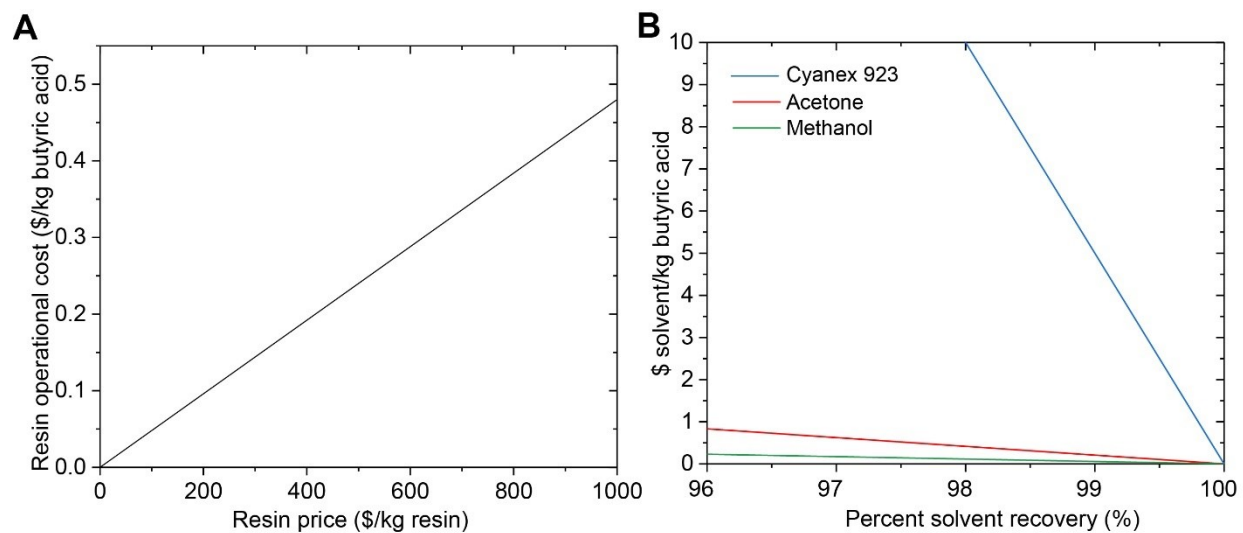
Figure S8. Operational cost sensitivity
(A) Resin operational cost on a per kg butyric acid product basis as a function of resin raw material price and (B) Solvent operational cost on a per kg butyric acid product basis as a function of percent solvent recovery from the distillation process.
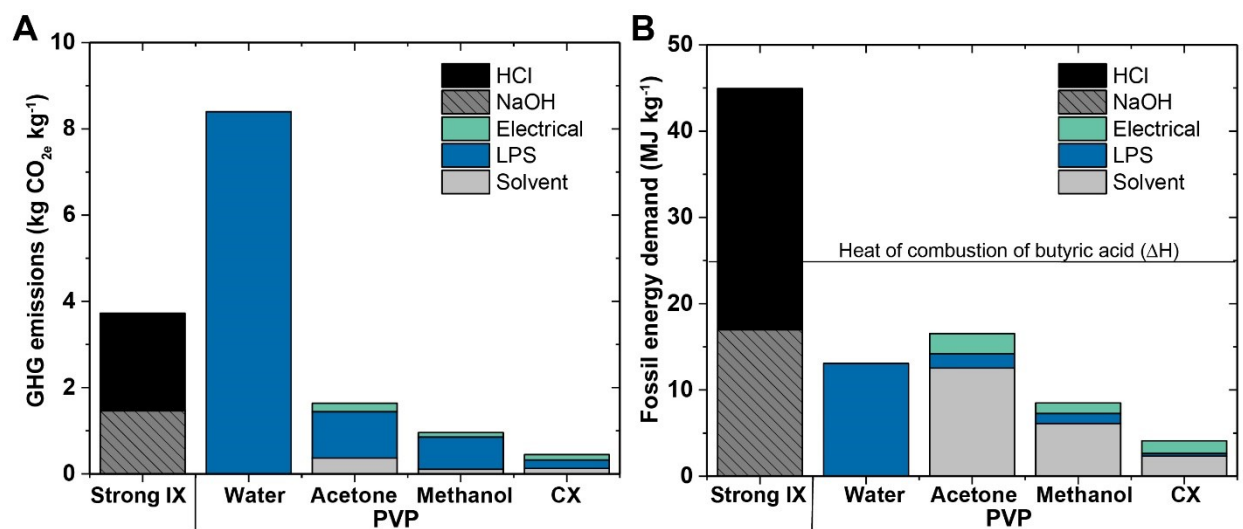
Figure S9. Environmental Impacts of the WBA and Strong IX Processes
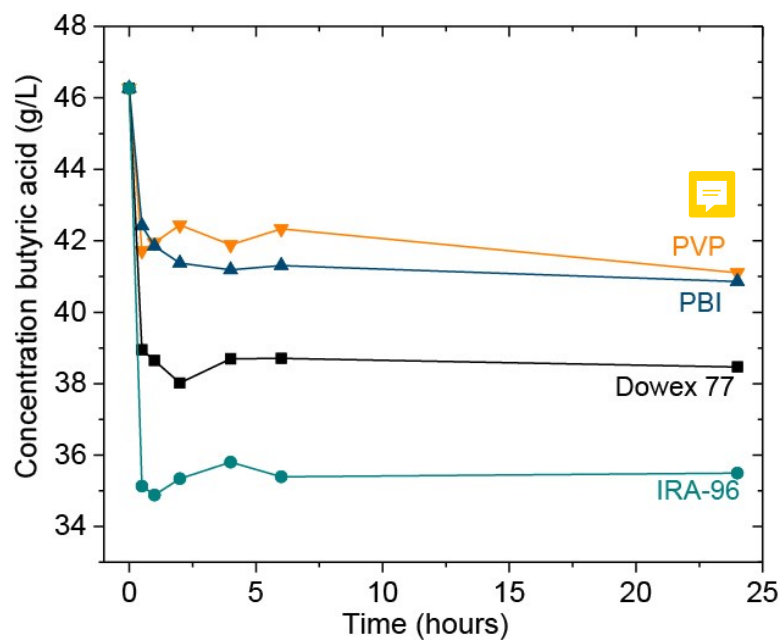(A) Fossil energy demand and (B) The GHG emission of the WBA processes compared with the strong IX process.

Figure S10. Kinetics of butyric acid adsorption by resins
The butyric acid concentration in the aqueous phase is shown as a function of time to probe the time needed to reach equilibrium. Within two hours, the concentration of butyric acid in the aqueous phase was within 10% of the concentration at 24 hours. A 24-hour benchmark equilibration time for all sample was used throughout the manuscript.
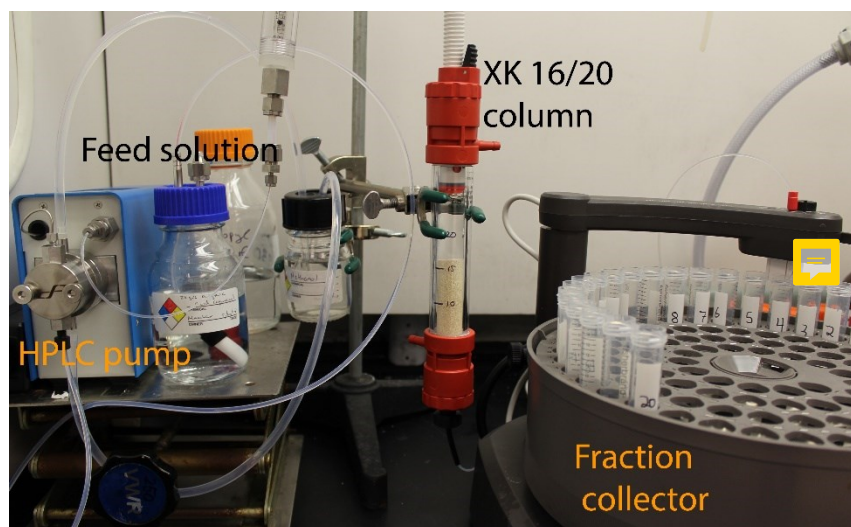
Figure S11. Photo of Fixed-bed Column System

Aspen Plus Simulations

Thermodynamic Property Methods
The UNIFAC property method was used to estimate thermodynamic properties of butyric acid and water as experimental data provided by Aspen Plus was inaccurate and could not be fit to a nonrandom two-liquid (NRTL) equation-of-state. Functional groups for each component were identified and specified in each simulation. A T_{XY} diagram was generated using the UNIFAC property method for butyric acid and water and is plotted in Figure S10.
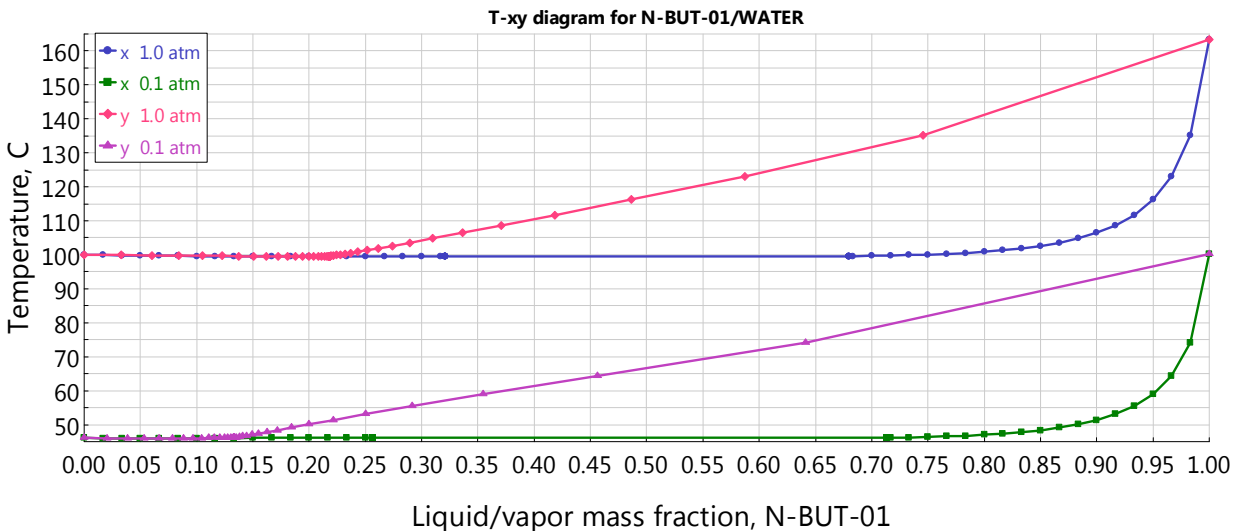
T-xy diagram for N-BUT-01/WATER

Legend:
- x 1.0 atm
- x 0.1 atm
- y 1.0 atm
- y 0.1 atm

Y-axis: Temperature, C
X-axis: Liquid/vapor mass fraction, N-BUT-01

Figure S12. T_{XY} diagram for butyric acid and water at 1 atmosphere generated using the UNIFAC and function group assignment in Aspen Plus.

Process Flow Diagram

The process flow diagram for the acetone and methanol simulation is shown in Figures S5. The feed stream (1) contained varying amounts of butyric acid, acetone and water entering the flash drum (F1) at 20°C and the same pressure as the flash distillation. 5 wt. % water was added to the feed stream to simulate the residue water that is carried over from desorption. Water elution profile from the column depends on column operational parameters such as flow rate and product recovery, and ranges from a minimum of 7.6% in our data to below 1% in optimized SMB systems.[12] The flash drum pressure was set to achieve a 99% recovery of butyric acid in the bottoms. This enables the much of the solvent to bypass the first multi-stage distillation column where butyric acid is separated from water and residue solvent. The bottom stream of the flash (F1) was preheated via a heat exchanger (HX1) to preheat the stream (4) before entering the distillation column (D1). Countercurrent heat exchangers with a 10 K minimum approach temperature were used with the shortcut calculation method. The preheated stream (4) entered the above stage 1 of a 3 stage RADFRAC distillation column (D1) operating with a reflux ratio of 1.1 at a pressure of 0.1 atmospheres. The bottoms rate was optimized to ensure a >95% recovery and >99% purity of butyric acid in the distillate bottoms (6). The distillate stream (5) of the distillation column (D1) contained the remaining acetone and water remaining after the flash. The vaporized solvent from the flash (2) and the first distillation column (5) was then compressed to 0.25 atm for the acetone case (0.35 atm for methanol) using mechanical vapor recompression technology in order to supply enough heat to power the reboiler (HX3) of the solvent recovery column (D2). The condensed solvent entered the solvent recovery distillation column (D2) on stage 11 of 12 RADFRAC distillation column operating at a pressure of 0.25 atmospheres. The solvent recovery column was optimized by varying the reflux ratio and the split fraction (SPLIT) to achieve a >99% recovery and purity of the solvent. Pumps set to a discharge pressure of 1 atmosphere were added at the outlet process streams to ensure that the product, solvent, and waste streams were no longer under vacuum. In order to separate the majority of the methanol upfront, a 3 stage RADFRAC distillation was utilized in place of the flash (heat integration between the bottoms of the second distillation column and the reboiler of the first column was performed in order to utilize energy present in the system).

For the 10 wt.% Cyanex in acetone solvent case, there are additional process units in order to separate the four components. As seen in Figure S6, there is an additional column added to separate the Cyanex (TOA in Aspen Plus) from the acid. In this simulation, the feed stream with varying concentrations entered the flash drum set to 20°C and set to the flash drum pressure. The flash was optimized the same way as with the acetone/methanol cases. The bottoms stream containing butyric acid, TOA, and the remaining water and acetone was preheated using a heat exchanger (HX1) and entered the RADFRAC distillation column (D1) above stage 2 of 3 with a reflux ratio of 0.1 and a column pressure of 0.1 atmospheres. The distillate rate was optimized to recover the butyric acid in the distillate and >99% of the TOA in the bottoms. The distillate of column D1 entered on stage 3 of a 3 stage RADFRAC distillation column (D2). The column reflux ratio was 1.2 with a column pressure of 0.1 atmospheres. The distillate rate was optimized to recover > 95% of butyric acid with a >99% purity out the bottoms. The remaining solvent in the distillate stream of the distillation column (D2) was compressed to 0.25 atmospheres in order to supply enough heat to power the reboiler (HX3) of the second solvent recovery column (D3). The stream (11) entered on stage 10 of a 12 stage RADFRAC distillation column at 0.25 atmospheres. The solvent recovery column (D3) was optimized by varying the reflux ratio and the split fraction (SPLIT) to achieve a >99% recovery and purity of the solvent. Pumps set to a discharge pressure of 1 atmosphere were added at the outlet process streams to ensure that the product, solvent, and waste streams were no longer under vacuum.

Energy Input Determination

Heating and cooling duties for each of the unit operations were reported by Aspen Plus. Vacuum pump duties were calculated manually using the following isentropic equation assuming a vacuum pump efficiency of 0.5 as these values are not calculated by Aspen Plus.

$$w_{in} = \left(\frac{1}{\eta_C}\right)\left(\frac{kRT_1}{k-1}\right)\left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$$

where:

w_{in}: Vacuum pump net work in $\frac{kJ}{mol}$ of evacuated gas

η_C: Pump efficiency

k: Heat capacity ratio $\left(\frac{C_p}{C_v}\right)$

R : Ideal gas constant in $\frac{kJ}{mol * K}$

T_1 : Temperature at the inlet of the vacuum pump in degrees Kelvin

P_2 : Pressure at the inlet of the vacuum pump

P_1 : Discharge pressure of the vacuum pump

For each simulation, the heat capacity ratio and temperature of the distillates were calculated by Aspen plus. The work per mole of gas evacuated calculated from this equation was then multiplied by the molar flow rate of the distillate stream to determine the energy required per hour of operation.

All energy inputs (heating, cooling, and vacuum) were then normalized to the production rate of butyric acid to achieve an energy input of MJ per kilogram of pure butyric acid distilled.

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