Supplementary Information (SI) for Green Chemistry.

Supplementary Information

Sustainable Potassium Sorbate Production from Triacetic Acid Lactone in Food-grade Solvents

Min Soo Kim[1,2], Sarang S. Bhagwat[2,3], Leoncio Santiago-Martínez[1,2], Xiaolei Shi[1], Kyuhyeok Choi[1], Jeremy S. Guest[2,3], and George W. Huber[1,2]*

[1]Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA

[2]DOE Center for Advanced Bioenergy and Bioproducts Innovation (CABBI), University of Illinois Urbana-Champaign, 1206 W. Gregory Drive, Urbana, IL 61801, USA

[3]Department of Civil and Environmental Engineering, University of Illinois Urbana-Champaign, 3221 Newmark Civil Engineering Laboratory, 205 N. Mathews Avenue, Urbana, IL 61801, USA

*Corresponding author; email: gwhuber@wisc.edu

Table S1. CO uptake and dispersion of Pd and Ni catalysts

Catalyst	CO uptake (μmol g^{-1})	Dispersion (%)
Pd/Al_2O_3	63.1	33.6
Ni/Si-Al	290.8	2.6
Ni/SiO_2	264.6	2.4

Table S2. Estimated reaction kinetic parameters for PSA production over Amberlyst 70 in IPA

Reaction	Temp. (℃)	*k'* (min^{-1})	Ea (kJ/mol)	lnA
HMP etherification (k_1)	100	0.0524	68.1±15.3	18.8±4.6
	130	0.151		
	160	1.131		
IHMP hydrolysis (k_2)	100	0.0142	74.4±1.4	19.7±0.3
	130	0.084		
	160	0.392		
HMP decomposition (k_3)	100	0.0091	51.8±8.5	11.9±2.5
	130	0.023		
	160	0.094		
IHMP decomposition (k_4)	100	0.000035	61.5±3.9	9.5±1.2
	130	0.000132		
	160	0.00055		
PSA decomposition (k_5)	100	0.00006	67.7±1.3	12.2±0.4
	130	0.00032		
	160	0.00138		

95% confidence interval in parameter estimation. 1^{st} order rate parameters that are lumped with the amount of Amberlyst 70. *k*=*k'*[g of Amberlyst 70]

Table S3. Assumed composition of feed sugarcane modeled to be consistent with Bhagwat et al.[1]

Component	**Composition (wt%)**
water	70
glucose	1.21
sucrose	13.7
lignin	3.28
ash	0.6
cellulose	6.12
hemicellulose	3.61
solids	1.5

Table S4. List of major units and equipment included in the biorefinery.

Process	ID	Unit	Equipment	Sources
Feedstock juicing	U201	crushing mill	crushing mill	Ref[2]
	U202	conveying belt	conveying belt	Ref[2]
	M201	mixer	mixer	BioSTEAM
	S201	vibrating screen	vibrating screen	Ref[2]
	T202	storage tank	tank	BioSTEAM
	H201	heat exchanger	floating head	BioSTEAM
	T203	mix tank	tank	BioSTEAM
	P201	pump	pump, motor	BioSTEAM
	T204	mix tank	tank	BioSTEAM
	T205	mix tank	tank	BioSTEAM
	P202	pump	pump, motor	BioSTEAM
	M202	mixer	mixer	BioSTEAM
	H202	heat exchanger	floating head	BioSTEAM
	T206	mix tank	tank	BioSTEAM
	C201	clarifier	clarifier	BioSTEAM
	C202	rotary vacuum filter	vessels, vacuum system - liquid-ring pump, oil seal, vacuum system	Ref[2]
	P203	pump	pump, motor	BioSTEAM
Fermentation	F301	multi-effect evaporator	condenser, mixer, vacuum system, evaporators	BioSTEAM
	F301 P	pump	pump, motor	BioSTEAM
	H301	heat exchanger	floating head	BioSTEAM
	M304	mix tank	tank	BioSTEAM
	M304 H	heat exchanger	double pipe	BioSTEAM
	R302	batch co fermentation	heat exchangers, reactors, agitators, cleaning in place, recirculation pumps	Ref[1]
	R303	seed train	pumps, agitators, reactors, heat exchangers	Ref[1]
	T301	seed hold tank	pump, agitator, tank	BioSTEAM
	K301	isothermal compressor	compressors	BioSTEAM
	V301	valve	valve	BioSTEAM

	M401	liquids mixing tank	turbine agitator, vertical pressure vessel, platform and ladders	BioSTEAM
	H401	heat exchanger	floating head	BioSTEAM
	M402	liquids mixing tank	turbine agitator, vertical pressure vessel, platform and ladders	BioSTEAM
	S401	solids centrifuge	centrifuges	BioSTEAM
	F401	multi-effect evaporator	condenser, mixer, vacuum system, evaporators	BioSTEAM
	F401 P0	pump	pump, motor	BioSTEAM
Separation	F401 P1	pump	pump, motor	BioSTEAM
	C401	crystallizer	crystallizer	BioSTEAM
	S402	solids centrifuge	centrifuges	BioSTEAM
	F402	drum dryer	drum dryer	BioSTEAM
	F403	multi-effect evaporator	condenser, mixer, vacuum system, evaporators	BioSTEAM
	F403 P0	pump	pump, motor	BioSTEAM
	F403 P1	pump	pump, motor	BioSTEAM
	H420	heat exchanger	double pipe	BioSTEAM
	M401	liquids mixing tank	turbine agitator, vertical pressure vessel, platform and ladders	BioSTEAM
	M405	mixer	mixer	BioSTEAM
	R401	hydrogenation reactor	vertical pressure vessel, platform and ladders, Nickel-silica-alumina catalyst, heat exchanger - floating head, recirculation pump, agitator, heat exchanger, vacuum system, recirculation pump, agitator, nickel-alumina-silica catalyst, scaler	BioSTEAM, Tables S5 and S6
Upgrading	R401_CR	pressure filter	dry air pressure filter, pressing air pressure filter, dry air compressor receiver tank, cloth wash pump, pressing air compressor receiver tank, pressure filter, wet cake conveyor, wet cake screw, recycled water tank, manifold flush pump, stillage tank, feed pump, filtrate tank, discharge pump, filtrate tank agitator	BioSTEAM
	R402	etherification and hydrolysis reactor	vertical pressure vessel, platform and ladders, Amberlyst-70 catalyst, heat exchanger - floating head, recirculation pump, agitator, heat exchanger, vacuum system, recirculation pump, agitator, Amberlyst-70 catalyst, scaler	BioSTEAM, Tables S5 and S6
	R402_CR	pressure filter	dry air pressure filter, pressing air pressure filter, dry air compressor receiver tank, cloth wash	BioSTEAM

			pump, pressing air compressor receiver tank, pressure filter, wet cake conveyor, wet cake screw, recycled water tank, manifold flush pump, stillage tank, feed pump, filtrate tank, discharge pump, filtrate tank agitator	
	R403	ring-opening hydrolysis reactor	vertical pressure vessel, platform and ladders, heat exchanger - floating head, recirculation pump, agitator, heat exchanger, vacuum system, recirculation pump, agitator, scaler	BioSTEAM, Tables S5 and S6
	R403_P	pump	pump, motor	BioSTEAM
	F404	drum dryer	drum dryer	BioSTEAM
	H410	heat exchanger	floating head	BioSTEAM
	F404_P	conveying belt	conveying belt	BioSTEAM
	F406	drum dryer	drum dryer	BioSTEAM
	F406_P	conveying belt	conveying belt	BioSTEAM
	M406	mixer	mixer	BioSTEAM
	F405	drum dryer	drum dryer	BioSTEAM
	H408	heat exchanger	floating head	BioSTEAM
	M408	mixer	mixer	BioSTEAM
Wastewater	M501	mixer	mixer	BioSTEAM
	M502	mixer	mixer	BioSTEAM
	U501	internal circulation reactor	tank, heat exchangers effluent pump, sludge pump	BioSTEAM, Ref[3]
	U502	anaerobic membrane bioreactor	tank, membrane, pumps, air pipes, blowers, degassing membrane, heat exchangers	BioSTEAM, Ref[3]
	U503	polishing filter	tank, packing polymers, pumps, degassing membrane, heat exchangers	BioSTEAM, Ref[3]
	U504	belt thickener	thickeners, effluent pump, sludge pump	BioSTEAM, Ref[3]
	C501	sludge centrifuge	centrifuges, effluent pump, sludge pump	BioSTEAM, Ref[3]
	M503	mixer	mixer	BioSTEAM
	M504	mixer	mixer	BioSTEAM
	U505	biogas upgrading	biogas upgrading unit	BioSTEAM, Ref[3]
	U506	reverse osmosis	evaporator, reactor	BioSTEAM, Ref[3]
Facilities	M901	mixer	mixer	BioSTEAM
	T601	CSL storage tank	tank	BioSTEAM

T601 P	pump	pump, motor	BioSTEAM
T607	sodium acetate storage tank	tank	BioSTEAM
T607 P	conveying belt	conveying belt	BioSTEAM
T608	acetylacetone storage tank	tank	BioSTEAM
T608 P	pump	pump, motor	BioSTEAM
T609	DAP storage tank	tank	BioSTEAM
T609 P	pump	pump, motor	BioSTEAM
T602	H_2 storage tank	tank	BioSTEAM
T603	KOH storage tank	tank	BioSTEAM
T603_P	conveying belt	conveying belt	BioSTEAM
T605	isopropanol storage tank	tank	BioSTEAM
T605_P	pump	pump, motor	BioSTEAM
T611	nickel-alumina-silica catalyst storage tank	tank	BioSTEAM
T611_P	conveying belt	conveying belt	BioSTEAM
T612	Amberlyst-70 catalyst storage tank	tank	BioSTEAM
T612_P	conveying belt	conveying belt	BioSTEAM
T620	KS storage tank	tank	BioSTEAM
T620 P	pump	pump, motor	BioSTEAM
CWP802	chilled water package	chilled water package	BioSTEAM
BT701	boiler turbogenerator	baghouse bags, boiler, deaerator, amine addition package, hot process water softener system, turbogenerator	BioSTEAM
CT801	cooling tower	cooling tower, cooling water pump	BioSTEAM
CWP803	chilled brine package	chilled brine package	BioSTEAM
HXN1001	heat exchanger network	heat exchangers	BioSTEAM
CIP901	CIP Package	clean-in-place package	BioSTEAM

	ADP902	air distribution package	plant air compressor, instrument air dryer, plant air receiver	BioSTEAM
	FWT903	fire water tank	pump, tank	BioSTEAM
	PWC904	process water center	tank, process water pump, makeup water pump	BioSTEAM

Table S5. List of parameters included in uncertainty and sensitivity analyses for the current state-of-technology for IPA (*IPA* scenario). Note all chemical prices were converted to the TEA year, 2019 (conversion method detailed in the script[4]). Samples with >100% total conversion of glucose, sucrose, and acetate were capped to 100% total conversion with the following priority order for sample product yields: TAL, citric acid, and cell mass (*Y. lipolytica*) following the assumptions in Bhagwat et al.[1]

Parameter name	Units	Base-line	Distribution Shape	Lower	Most Common	Upper	References
			TEA				
plant annual operating days	d	180	triangular	120	180	240	from Ref[2,5] for sugarcane (lower, most common, baseline) and integrated sweet sorghum (upper)
feedstock unit price	$·wet-kg^{-1}	0.0345	triangular	0.0276	0.0345	0.0414	baseline from Ref[2]; bounds are baseline ±20%
natural gas unit price	$·kg^{-1}	0.2765	triangular	0.2163	0.2765	0.3321	minimum, mean, and maximum price during 2010-2019[6]
electricity unit price	$·kWh^{-1}	0.07	triangular	0.067	0.07	0.074	minimum, mean, and maximum price during 2010-2019[6]
sodium acetate unit price	$·kg-acetic-acid-eq.$^{-1}$	1.3691	triangular	0.931	1.369	1.808	minimum, mean, and maximum price in 2008[7]
CSL unit price	$·kg^{-1}	0.0747	triangular	0.05976	0.0747	0.08964	baseline from Ref[8]; bounds are baseline ±20%
DAP unit price	$·kg^{-1}	0.6876	uniform	0.28271		1.0924	bounds from Ref[7,9]; baseline is mean of bounds
federal corporate tax rate	%	21.0	uniform	15.0		28.0	baseline from Ref[10]; bounds based on Ref[11,12]
internal rate of return	%	10.0	uniform	8.0		12.0	baseline for consistency with Ref[2,9]; bounds are baseline ±20%
IPA unit price	$·kg^{-1}	1.069	uniform	0.994		1.281	bounds (minimum and maximum) and baseline (mean of bounds) from 2022-2024 range reported by Ref[13]
KOH unit price	$·kg^{-1}	1.60	uniform	1.28		1.92	baseline from Ref[14]; bounds are baseline ±20%
nickel-silica-alumina catalyst unit price	$·kg^{-1}	33	triangular	5	33	50	baseline and bounds are the mean, minimum, and maximum of largest-order prices from vendor

							listings for high-purity nickel, Raney nickel, and nickel-alumina alloys[15-19]
Amberlyst-70 catalyst unit price	$\$\cdot kg^{-1}$	1.442	triangular	1	1.442	2.1	baseline and bounds are the mean, minimum, and maximum of largest-order prices from vendor listings for Amberlyst-15[20-28]
desired annual KS production	pure metric ton/y	15944	triangular	12755	15944	19133	baseline described in the *Materials and Methods* section of the manuscript; bounds are baseline ±20%
Fermentation							
fermentation CSL loading	$g\cdot L^{-1}$	76.903	uniform	41.707		101.9	baseline and bounds from Ref[1]
fermentation DAP loading	$g\cdot L^{-1}$	10.228	uniform	5.547		14.909	baseline and bounds from Ref[1]
fermentation sodium acetate loading	g-acetic-acid-eq.$\cdot L^{-1}$	10.0	uniform	8.0		12.0	baseline from Ref[29]; bounds are baseline ±20%
fermentation aeration rate safety factor	%	100	uniform	50		200	baseline and bounds from Ref[1]
seed train fermentation ratio	%	95.0	uniform	90.0		100.0	baseline based on Ref[9]; bounds mirror the difference between the baseline and the maximum possible value (100.0%)
inoculum ratio	%	7.0	uniform	6.3		7.7	baseline based on Ref[9]; bounds are ±10%
fermentation TAL yield	% theoretical	40.48	uniform	32.38		48.58	baseline from Ref[29]; bounds are baseline ±20%
fermentation TAL titer	$g\cdot L^{-1}$	35.9	uniform	28.72		43.08	baseline from Ref[29]; bounds are baseline ±20%
fermentation TAL productivity	$g\cdot L^{-1}\cdot h^{-1}$	0.120	uniform	0.096		0.144	baseline from Ref[29]; bounds are baseline ±20%
fermentation *Yarrowia lipolytica* yield	g-cells$\cdot$g-glucose-eq^{-1}	0.339	uniform	0.271		0.407	baseline from Ref[29]; bounds are baseline ±20%
fermentation citric acid yield	% theoretical	8.86	uniform	7.08		10.6	based on concentrations reported in Ref[29]
Separation							

TAL ring-opening decarboxylation conversion	% theoretical	20.9	uniform	4.63		34.0	range observed experimentally in this work; Table S5
TAL solubility multiplier	%	1	uniform	0.8		1.2	baseline is from equation (III); bounds are baseline ±20%
crystallization time	h	8	uniform	2		14	assumed
centrifuge solids recovery	%	95.0	uniform	90.0		100.0	baseline from Ref[30]; bounds mirror the difference between the baseline and the maximum possible value (100.0%)
centrifuge moisture retention	%	50.0	uniform	40.0		60.0	baseline from Ref[30]; bounds are baseline ±20%
dryer moisture retention	%	5.00	uniform	4.00		6.00	baseline from Ref[30]; bounds are baseline ±20%
Upgrading							
hydrogenation catalyst NiSiO2:TAL ratio	$kg \cdot kg^{-1}$	0.2	uniform	0.18		0.22	baseline from this work; bounds are baseline ±10%
hydrogenation reaction time	h	9.4	uniform	8.5		10.3	
hydrogenation temperature	°C	100	uniform	90		110	
hydrogenation pressure	Pa	3500000	uniform	3150000		3850000	
hydrogenation TAL-to-HMP conversion	%	96.9	uniform	93.8		100.0	baseline from this work; bounds mirror the difference between the baseline and the maximum possible value (100.0%)
hydrogenation spent catalyst NiSiO2 replacement rate	y^{-1}	1.0	uniform	0.1		1.9	baseline and bounds assumed; bounds represent a wide range to characterize a large uncertainty
etherification & hydrolysis catalyst Amberlyst70:HMTHP ratio	$kg \cdot kg^{-1}$	0.5	uniform	0.45		0.55	baseline from this work; bounds are baseline ±10%
etherification & hydrolysis reaction time	h	6.1	uniform	5.5		6.7	
etherification & hydrolysis temperature	°C	160	uniform	144		176	

etherification & hydrolysis HMTHP-to-PSA conversion	%	87.1	uniform	78.4		95.8	
etherification & hydrolysis pressure	Pa	2000000	uniform	1800000		2200000	
etherification & hydrolysis spent catalyst Amberlyst70 replacement rate	y^{-1}	1	uniform	0.1		1.9	baseline and bounds assumed; bounds represent a wide range to characterize a large uncertainty
ring-opening & hydrolysis reaction time	h	19.0	uniform	17.1		20.9	baseline from this work; bounds are baseline ±10%
ring-opening & hydrolysis PSA-to-KS conversion	%	99.9	uniform	99.8		100.0	baseline from this work; bounds mirror the difference between the baseline and the maximum possible value (100.0%)
ring-opening & hydrolysis temperature	°C	130	uniform	117		143	baseline from this work; bounds are baseline ±10%
ring-opening & hydrolysis pressure	Pa	2000000	uniform	1800000		2200000	
upgrading IPA:TAL mass ratio	kg-IPA·kg-TAL^{-1}	31.392	uniform	28.2528		34.5312	
purification IPA:KS mass ratio	kg-IPA·kg-KS^{-1}	31.545	uniform	28.3905		34.6995	
Facilities							
product KS storage time	h	168	triangular	134.4	168	201.6	baseline based on Ref[9]; bounds are baseline ±20%
boiler efficiency	%	80.0	uniform	72.0		88.0	baseline from Ref[31,32]; bounds are baseline ±10% based on Ref[8]
turbogenerator efficiency	%	85.0	uniform	76.5		93.5	baseline from Ref[30]; bounds are baseline ±10%

Table S6. List of parameters changed relative to the relative to the current state-of-technology IPA scenario (*IPA*; Table S5) in uncertainty analyses for three scenarios: *catalysis improv.*, *all-round improv.*, and *THF & EtOH* (**Fig. 8**). In addition, for the *catalysis improv.* and *all-round improv.* scenarios, the hydrogenation, etherification and hydrolysis, and ring-opening and hydrolysis reactors were assumed to operate in continuous mode rather than batch mode. Samples with >100% total conversion of glucose, sucrose, and acetate were capped to 100% total conversion with the following priority order for sample product yields: TAL, citric acid, and cell mass (*Y. lipolytica*) following the assumptions in Bhagwat et al.[1]

Parameter name	Units	Base-line	Distribution Shape	Lower	Most Common	Upper	References
catalysis improv. and *all-round improv.*							
etherification & hydrolysis HMTHP-to-PSA conversion	%	96.9	uniform	93.8		100.0	baseline and bounds assumed based on baseline conversion for hydrogenation and baseline reaction time for etherification & hydrolysis (Table S5; see *Techno-economic analysis and life cycle assessment of biorefineries producing KS via TAL from sugarcane* in the *Results and Discussion* section in the manuscript)
hydrogenation reaction time	h	6.1	uniform	5.5		6.7	
ring-opening & hydrolysis reaction time	h	6.1	uniform	5.5		6.7	
all-round improv.							
desired annual KS production	pure metric ton·y^{-}	13385.2	triangular	14295	17869	21443	maintained to be same as for the *IPA* scenario (Table S6)
plant annual operating days	d	240	triangular	150	240	300	baseline and bounds are consistent with Ref[1]
fermentation TAL yield	% theoretical	73.0	uniform	58.4		87.6	
fermentation TAL titer	g·L^{-1}	65.0	uniform	52.0		78.0	
TAL ring-opening decarboxylation conversion	% theoretical	4.8	uniform	1.1		7.8	
pH maintained before heating	n/a	11.0	uniform	10.0		12.0	
THF & EtOH							
THF unit price	$\$\cdot kg^{-1}$	4.45	uniform	4.25		4.66	baseline and bounds from Ref[7]
ethanol unit price	$\$\cdot kg^{-1}$	0.740	triangular	0.46	0.740	0.939	baseline, lower bound, and upper bound are mean, minimum, and maximum of 2010-2019 range reported by Ref[6]
hydrogenation reaction time	h	1.2	uniform	1.08		1.32	baseline from this work; bounds are baseline ±10%
hydrogenation	%	97.2	uniform	94.4		100.0	baseline from this work; bounds

TAL-to-HMP conversion							mirror the difference between the baseline and the maximum possible value (100.0%)
etherification & hydrolysis reaction time	h	8.9	uniform	8.0		9.8	baseline from this work; bounds are baseline ±10%
etherification & hydrolysis HMTHP-to-PSA conversion	%	86.5	uniform	77.8		95.1	
ring-opening & hydrolysis reaction time	h	8.0	uniform	7.2		8.8	
ring-opening & hydrolysis PSA-to-KS conversion	%	99.9	uniform	98.0		100.0	baseline from this work; bounds assumed

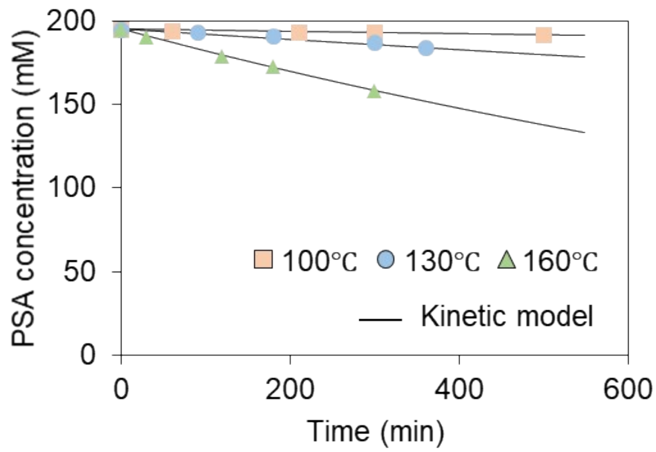


Fig. S1. Experimental data vs. kinetic model for PSA degradation over Amberlyst 70 at 100℃, 130℃, and 160℃. Reaction conditions: Batch reactor, PSA (37 mM) in 25 mL IPA solvent, Mass ratio catalyst: HMP = 1:1, 30 bar Ar. The rate constant (k_5, min^{-1}) of the PSA degradation at 100℃, 130℃, and 160℃ was measured to be $3.36\times10^{-5}\pm4.07\times10^{-6}$, $1.62\times10^{-4}\pm1.17\times10^{-5}$, and $6.90\times10^{-4} \pm 4.63\times10^{-5}$, respectively.

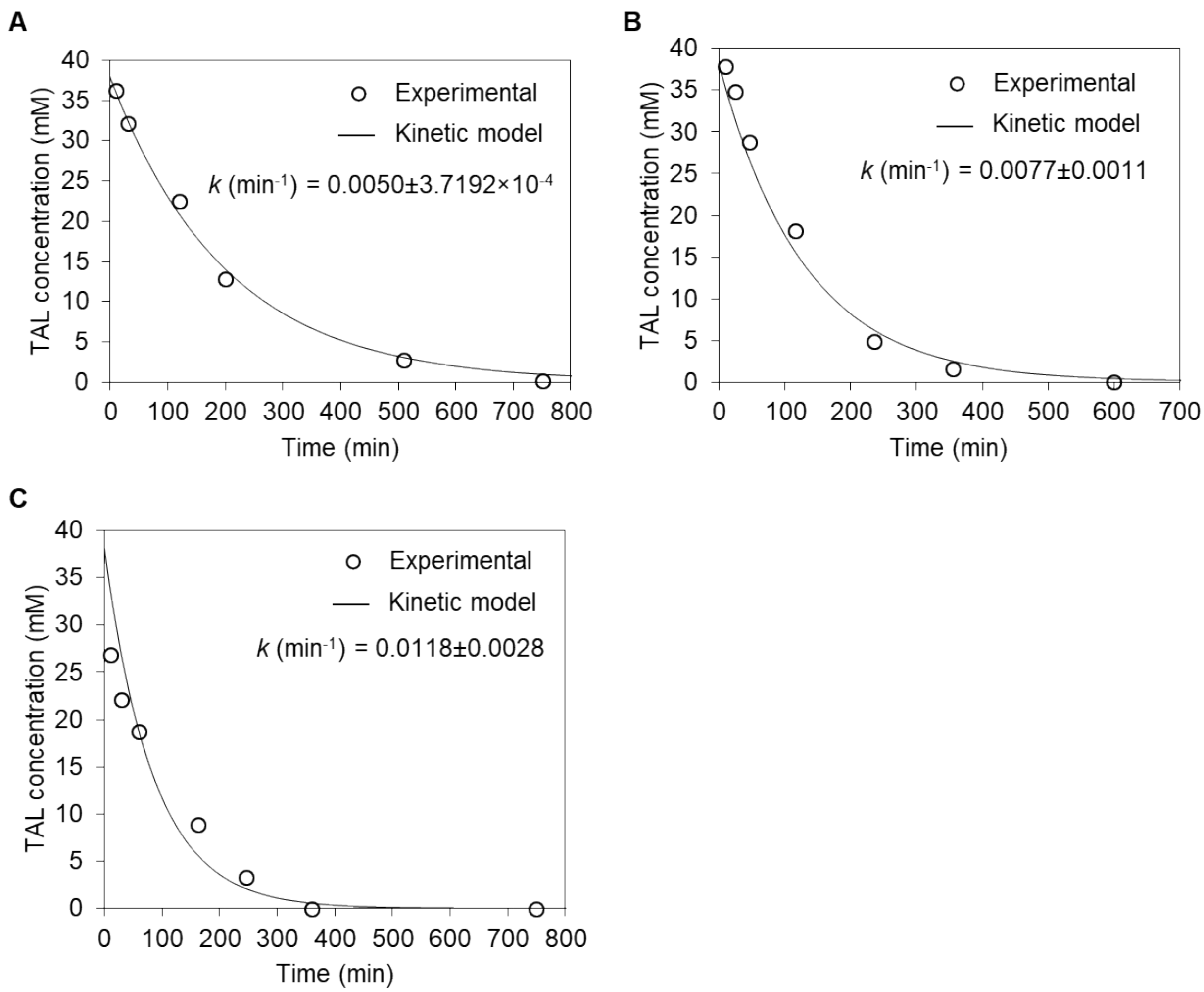


Fig. S2. Experimental data vs. kinetic model for TAL consumption over Ni/Si-Al in (A) EtOH, (B) IPA, and (C) THF. Reaction conditions: batch reactor, TAL (38.2-39.1 mM) in 25 mL of solvent, Mass ratio catalyst: TAL = 1:5, 100℃, 30 bar H_2.

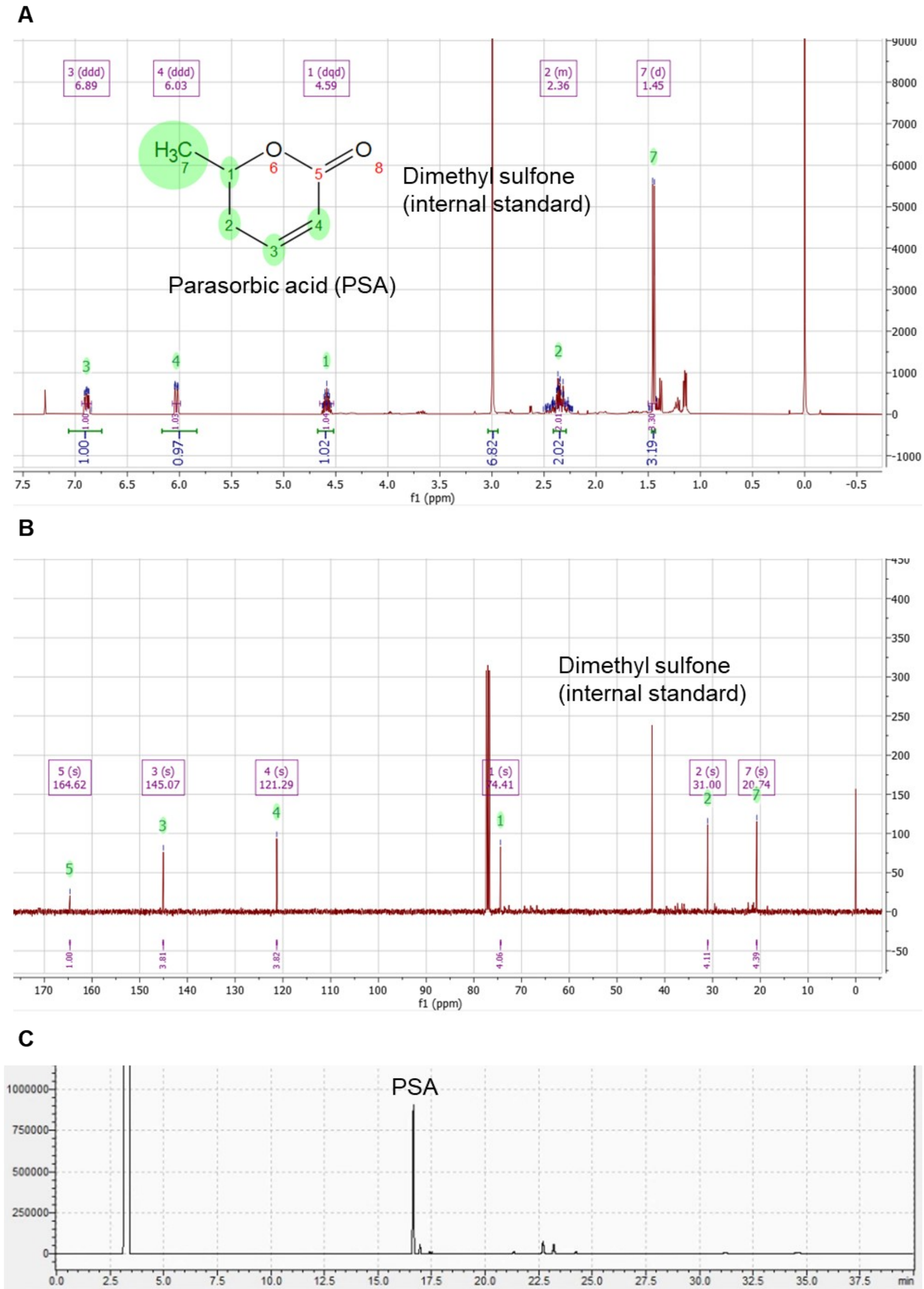
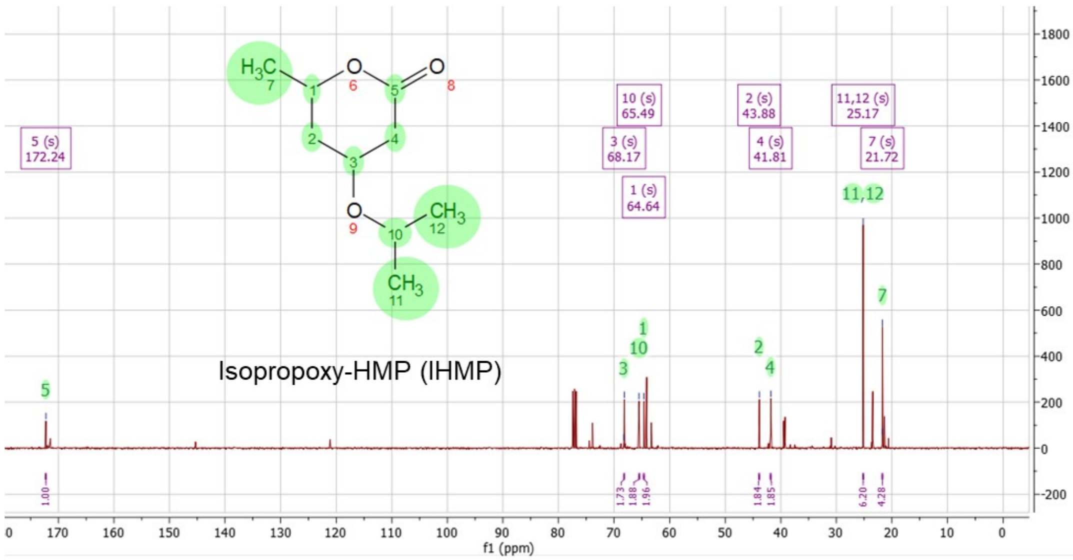


Fig. S3. (A) ^{1}H NMR spectra, (B) ^{13}C NMR spectra, and (C) GC-FID spectra of PSA synthesized from HMP in IPA over Amberlyst 70.

A



B

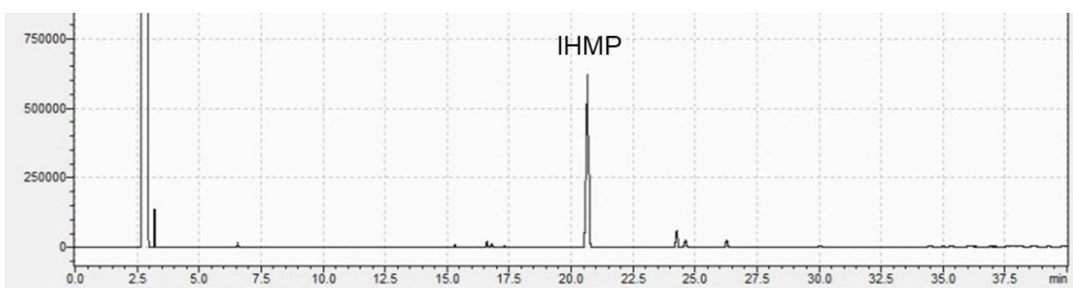
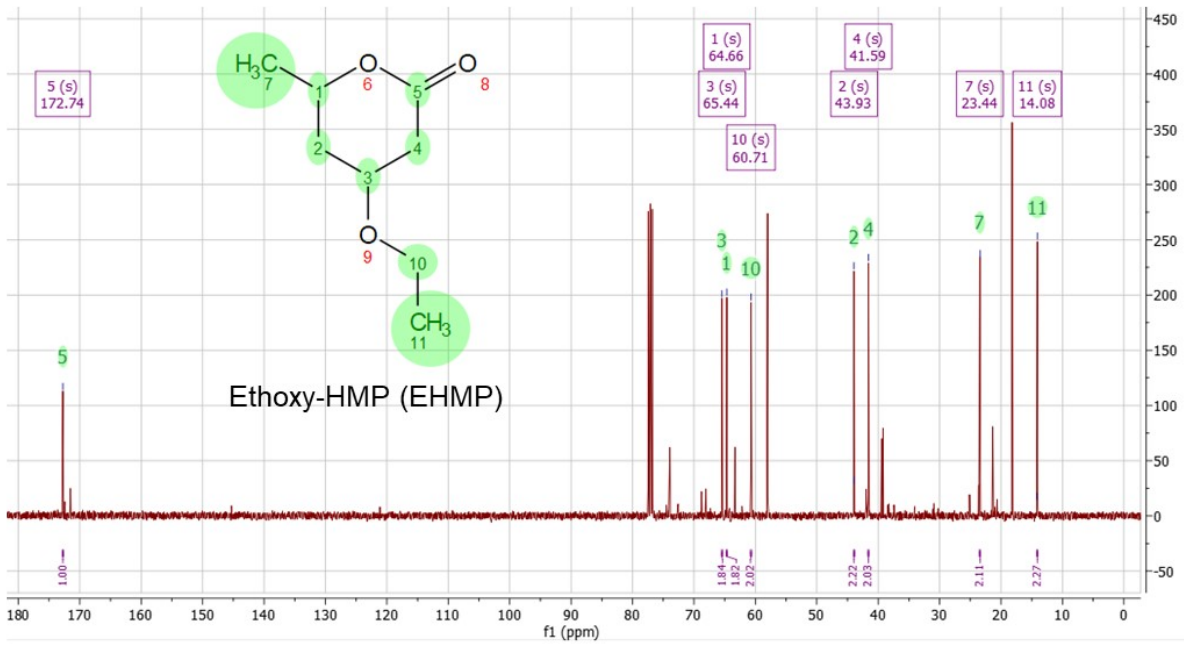


Fig. S4. (A) ^{13}C NMR spectra and (B) GC-FID spectra of IHMP synthesized from HMP in IPA over Amberlyst 70. A small amount of HMP and IPA is present in the NMR spectra.

A



B

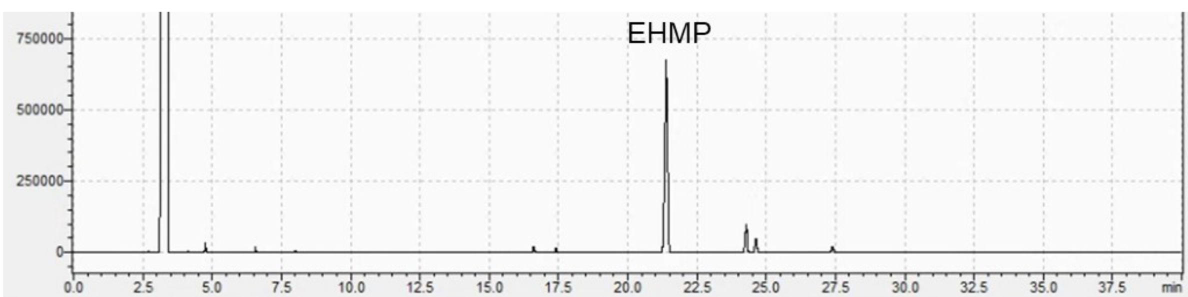


Fig. S5. (A) ^{13}C NMR spectra and (B) GC-FID spectra of EHMP synthesized from HMP in EtOH over Amberlyst 70. A small amount of HMP and EtOH is present in the NMR spectra.

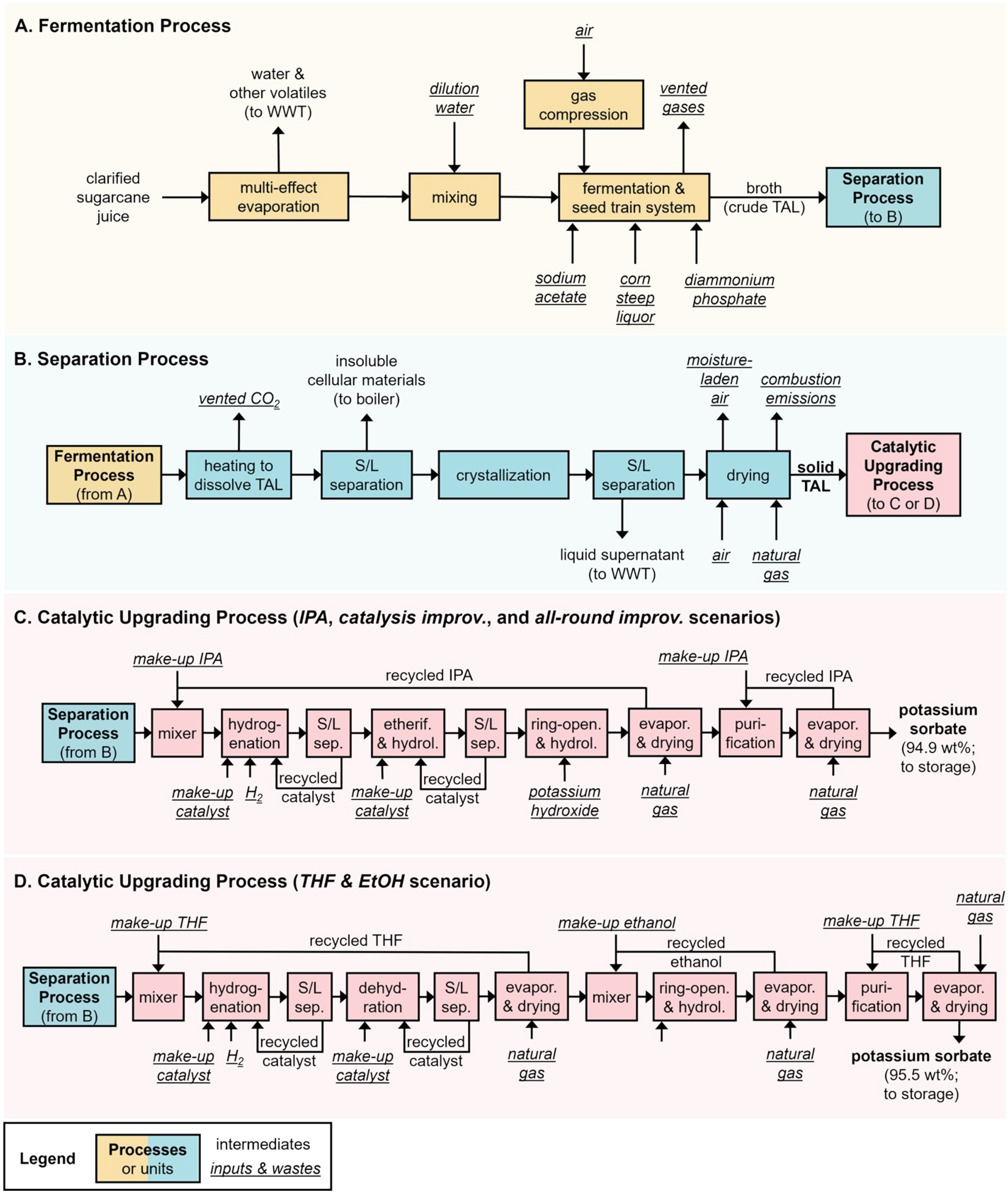


Fig. S6. Simplified block flow diagram for the (A) fermentation and (B) separation processes as in a previous study[1], (C) catalytic upgrading process using IPA solvent as in this study; and (D) catalytic upgrading process using THF and ethanol solvents as in a previous study[33]. *WWT* denotes wastewater treatment. The catalyst for hydrogenation was nickel-silica-alumina, the catalyst for etherification & hydrolysis (*etherif. & hydrol.*) was Amberlyst-70, and ring-opening & hydrolysis (*ring-open. & hydrol.*) proceeded without an added catalyst. Catalyst recovery was performed by solid-liquid separation (*S/L sep.*), and solvent recovery was performed using a multi-effect evaporator and drum dryer (*evapor. & drying*) where noted. Some units (e.g., pumps, mixers, splitters, heat exchangers) are not included in the figure for clarity; the process flow diagram in the system report (available in the online repository[4]) includes the full set of details.

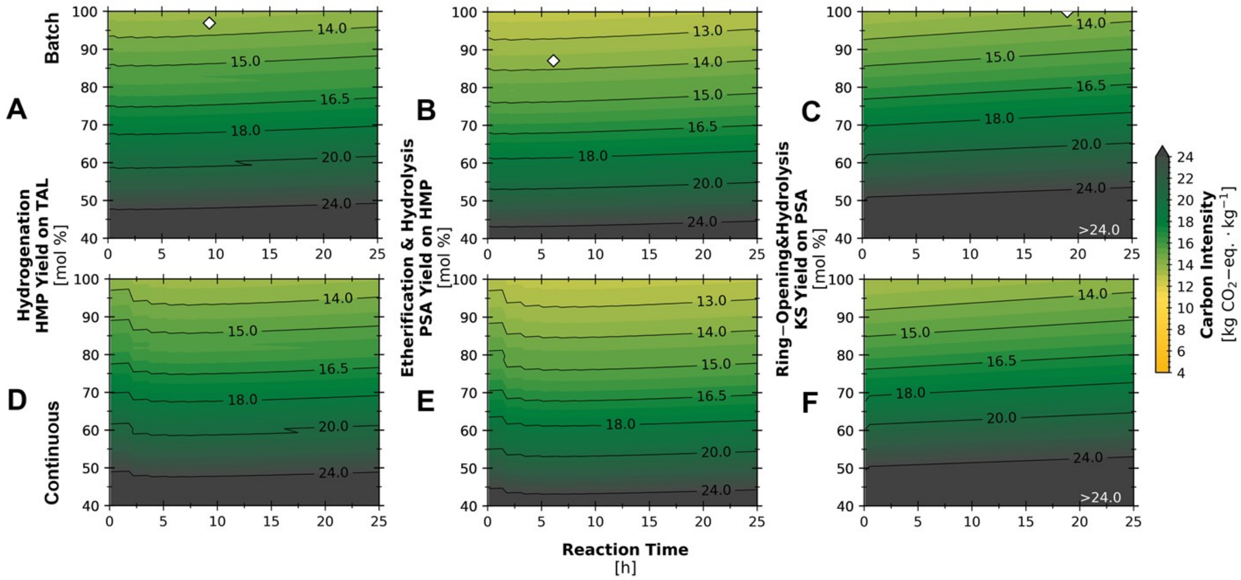


Fig. S7. Carbon intensity (CI) of KS across theoretical product yields (*y*-axes) and reaction times (*x*-axes) for the (A,D) hydrogenation, (B,E) etherification and hydrolysis, and (C,F) ring-opening and hydrolysis reactors operating in batch (A,B,C) and continuous modes (D,E,F). For a given point on the figure, the *x-axis* value represents the represents the reaction time (h), the *y-axis* value represents the yield (mol%) of HMP on TAL (A,D), PSA on HMP (B,E), or KS on PSA (C,F), and the color represents CI. The baseline product yield-reaction time combinations for each reactor are represented by diamonds (A,B,C).

MPSP
CI
Co-heat and power: Turbogenerator efficiency
Co-heat and power: Boiler efficiency
Storage: Product KS storage time
Upgrading: Purification ipa:ks mass ratio
Upgrading: Upgrading ipa:tal mass ratio
Upgrading: Ring-opening & hydrolysis pressure
Upgrading: Ring-opening & hydrolysis temperature
Upgrading: Ring-opening & hydrolysis psa-to-ks conversion
Upgrading: Ring-opening & hydrolysis reaction time
Upgrading: Etherification & hydrolysis spent catalyst amberlyst70 replacement rate
Upgrading: Etherification & hydrolysis pressure
Upgrading: Etherification & hydrolysis hmp-to-psa conversion
Upgrading: Etherification & hydrolysis temperature
Upgrading: Etherification & hydrolysis reaction time
Upgrading: Etherification & hydrolysis catalyst amberlyst70:hmp ratio
Upgrading: Hydrogenation spent catalyst ni si o2 replacement rate
Upgrading: Hydrogenation tal-to-hmp conversion
Upgrading: Hydrogenation pressure
Upgrading: Hydrogenation temperature
Upgrading: Hydrogenation reaction time
Upgrading: Hydrogenation catalyst ni si o2:tal ratio
Separation: Dryer moisture retention
Separation: Centrifuge moisture retention
Separation: Centrifuge solids recovery
Separation: Crystallization time
Separation: TAL solubility multiplier
Separation: TAL decarboxylation conversion
Fermentation: Fermentation citrate yield
Fermentation: Fermentation y. lipolytica yield
Fermentation: Fermentation TAL productivity
Fermentation: Fermentation TAL titer
Fermentation: Fermentation TAL yield
Fermentation: Inoculum ratio
Fermentation: Seed train fermentation ratio
Fermentation: Fermentation aeration rate safety factor
Fermentation: Fermentation acetate loading
Fermentation: Fermentation DAP loading
Fermentation: Fermentation CSL loading
TEA: Internal rate of return
TEA: Federal corporate tax rate
TEA: Desired annual production
TEA: Amberlyst-70 catalyst unit price
TEA: Ni-Si o2 catalyst unit price
TEA: KOH unit price
TEA: IPA unit price
TEA: DAP unit price
TEA: CSL unit price
TEA: Acetate unit price
TEA: Electricity unit price
TEA: Natural gas unit price
TEA: Feedstock unit price
TEA: Plant annual operating days
-1.00
-0.50
0.00
0.50
1.00
Spearman's ρ
0.00
0.50
1.00
p-value

Fig. S8. Sensitivity analysis results for the biorefinery in the *IPA* scenario as Spearman's rank order correlation coefficients (Spearman's ρ; x-axis, left; from -1.00 to 1.00) and corresponding p-values (x-axis, right; from 0.00 to 1.00) for MPSP, GWP_{100}, and FEC, with respect to each of 30 parameters included in the uncertainty analysis (y-axes). The vertical dashed gray line represents a p-value of 0.05.

References

1 S.S. Bhagwat, M.N. Dell'Anna, Y. Li, C. Mingfeng, E.C. Brace, S.S. Bhagwat, G.W. Huber, H. Zhao, J.S. Guest, ChemRxiv., 2024. doi:10.26434/chemrxiv-2024-4sz8x-v2. This content is a preprint and has not been peer-reviewed.

2 Y.R. Cortés-Peña, C. Kurambhatti, K. Eilts, V. Singh, J.S. Guest, *ACS Sustain. Chem. Eng.*, 2022, **10**, 13980–13990.

3 Y. Li, G.A. Kontos, D.V. Cabrera, N.M. Avila, T.W. Parkinson, M.B. Viswanathan, V. Singh, F. Altpeter, R.A. Labatut, J.S. Guest, *ACS Sustain. Chem. Eng.*, 2023, **11**, 3861-3872.

4 BioSTEAMDevelopmentGroup, Triacetic acid lactone biorefineries, (2024). https://github.com/BioSTEAMDevelopmentGroup/Bioindustrial-Park/tree/master/biorefineries/TAL (accessed June 17, 2024).

5 H. Huang, S. Long and V. Singh, *Biofuels, Bioprod. Bioref.*, 2016, **10**, 299-315.

6 U.S. Energy Information Administration, Annual Energy Outlook, (n.d.). https://www.eia.gov/outlooks/aeo/ (accessed June 17, 2024).

7 ICIS, Chemical Market Reporter, 2008. https://web.archive.org/web/20161125084558/http://www.icis.com:80/chemicals/channel-info-chemicals-a-z/ (accessed May 22, 2024).

8 Y. Li, S.S. Bhagwat, Y.R. Cortés-Peña, D. Ki, C.V. Rao, Y.-S. Jin, J.S. Guest, *ACS Sustain. Chem. Eng.*, 2021, **9,** 1341–1351.

9 D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, D. Dudgeon, Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: Dilute-acid pretreatment and enzymatic hydrolysis of corn stover, National Renewable Energy Laboratory (NREL), 2011. http://www.nrel.gov/docs/fy11osti/47764.pdf (accessed June 13, 2024).

10 Committee on Ways and Means, US house of representatives. *Hearings on H.R. 4120*, 74th Congress, 1st Session, 2018.

11 Office of Management and Budget (US), *Analytical Perspectives: Budget of the US Government, Fiscal Year 2024*, Government Publishing Office, Washington, DC, 2023.

12 G. Watson, The Tax Foundation, Trump Corporate Tax Rate Cut Proposal: Details & Analysis (2023). https://taxfoundation.org/blog/trump-corporate-tax-cut/ (accessed November 20, 2023).

13 CHEMANALYST, Isopropyl Alcohol (IPA) Price Trend and Forecast, (n.d.). https://www.chemanalyst.com/Pricing-data/isopropyl-alcohol-31 (accessed June 11, 2024).

14 Alibaba.com, Reagent Grade Caustic Potash Potassium Hydroxide, (n.d.). https://www.alibaba.com/product-detail/Reagent-Grade-90-caustic-potash-potassium_62118969650.html?spm=a2700.galleryofferlist.0.0.28555ed4pKlEVC&s=p (accessed March 25, 2024).

15 Alibaba.com, Pure 99 99.99 Ni Powdery High Quality Battery Iron Nickel Alloys Spherical Zirconium Price Nickel Powder CAS No 7440-02-0, (n.d.). https://www.alibaba.com/product-detail/Pure-99-99-99-Ni-Powdery_1600796014023.html?spm=a2700.galleryofferlist.normal_offer.d_title.b7d0154ab6qIRO (accessed June 11, 2024).

16 Alibaba.com, High purity nickel powder CAS: 7440-02-0 Electrolytic ultrafine Ni powder Non spherical nickel metal alloy powder Price, (n.d.). https://www.alibaba.com/product-detail/High-purity-nickel-powder-CAS-7440_1601043582452.html?spm=a2700.galleryofferlist.normal_offer.d_title.b7d0154ab6qIRO (accessed June 11, 2024).

17 Alibaba.com, Nickel Alumina modium catalyst cost Price raney nickel oxide methane based catalysts For oil Hydrogenation, (n.d.). https://www.alibaba.com/product-detail/Nickel-Alumina-modium-catalyst-cost-Price_62039092901.html?spm=a2700.galleryofferlist.normal_offer.d_title.31592650y6YlHm (accessed June 11, 2024).

18 Alibaba.com, High quality customized NiAl20 Raney nickel catalyst for hydrogen production by electrolysis of water, (n.d.). https://www.alibaba.com/product-detail/High-quality-customized-NiAl20-Raney-nickel_1601019811920.html?spm=a2700.galleryofferlist.normal_offer.d_title.31592650ztR5t4 (accessed June 11, 2024).

19 Alibaba.com, Customized design increase specific surface area NiAl50 Raney nickel catalyst for hydrogen production by electrolysis of water, (n.d.). https://www.alibaba.com/product-detail/Customized-design-increase-specific-surface-area_1601019920484.html?spm=a2700.galleryofferlist.normal_offer.d_title.31592650ztR5t4 (accessed June 11, 2024).

20 Alibaba.com, Ion exchange resin for MTBE equal to Amberlyst 15 wet, (n.d.). https://www.alibaba.com/product-detail/Ion-exchange-resin-for-MTBE-equal_62529933735.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

21 Alibaba.com, High Temperature Resistance Catalyst Resin equal to AMBERLYST DT, (n.d.). https://www.alibaba.com/product-detail/High-Temperature-Resistance-Catalyst-Resin-equal_62530999330.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

22 Alibaba.com, Chinese manufacturers Ion exchange resin for MTBE equal to Amberlyst 15 wet, (n.d.). https://www.alibaba.com/product-detail/Chinese-manufacturers-Ion-exchange-resin-for_1600848354148.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 22, 2024).

23 Alibaba.com, Purity 99% AMBERLYST(R) 15 with high quality CAS:9037-24-5, (n.d.). https://www.alibaba.com/product-detail/purity-99-AMBERLYST-R-15-with_1600342344644.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

24 Alibaba.com, AMBERLYST(R) 15 cas 9037-24-5 macroporous resin with low price, (n.d.). https://www.alibaba.com/product-detail/AMBERLYST-R-15-cas-9037-24_1600993084228.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

25 Alibaba.com, High Temperature Resistance Catalyst Resin equal to AMBERLYST A45, (n.d.). https://www.alibaba.com/product-detail/High-Temperature-Resistance-Catalyst-Resin-equal_62530910597.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

26 Alibaba.com, 99% AMBERLYST(R) 15 wet type Dry type AMBERLYST(R) 15 CAS 39389-20-3, (n.d.). https://www.alibaba.com/product-detail/99-AMBERLYST-R-15-wet-type_1600267306406.html?spm=a2700.galleryofferlist.normal_offer.d_title.22a24164j8EA7y (accessed May 25, 2024).

27 Chemical Book, AMBERLYST (R) 15, (n.d.). https://www.chemicalbook.com/ProductDetail_EN_451808.htm (accessed May 25, 2024).

28 Chemical Book, Amberlyst (R) 15, (n.d.). https://www.chemicalbook.com/ProductDetail_EN_916657.htm (accessed May 25, 2024).

29 K.A. Markham, C.M. Palmer, M. Chwatko, J.M. Wagner, C. Murray, S. Vazquez, A. Swaminathan, I. Chakravarty, N.A. Lynd, H.S. Alper, Rewiring yarrowia lipolytica toward triacetic acid lactone for materials generation, Proceedings of the National Academy of Sciences of the United States of America 115 (2018) 2096–2101. https://doi.org/10.1073/pnas.1721203115.

30 Y. Cortes-Peña, D. Kumar, V. Singh, J.S. Guest, BioSTEAM: A Fast and Flexible Platform for the Design, Simulation, and Techno-Economic Analysis of Biorefineries under Uncertainty, *ACS Sustain. Chem. Eng.*, 2020, **8**, 3302–3310.

31 D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, D. Dudgeon, Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: Dilute-acid pretreatment and enzymatic hydrolysis of corn stover, National Renewable Energy Laboratory (NREL), 2011. http://www.nrel.gov/docs/fy11osti/47764.pdf (accessed June 13, 2015).

32 R.E. Davis, N.J. Grundl, L. Tao, M.J. Biddy, E.C. Tan, G.T. Beckham, D. Humbird, D.N. Thompson, M.S. Roni, Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update, National Renewable Energy Laboratory (NREL), 2018. https://doi.org/10.2172/1483234.

33 M.S. Kim, D. Choi, J. Ha, K. Choi, J.-H. Yu, J.A. Dumesic, G.W. Huber, *ACS Catal.*, 2023, **13**, 14031–14041.