

## Supplementary Information

### Valorization of Aqueous Waste Streams from Thermochemical Biorefineries

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**Table S1:** Aqueous phase analysis from pine catalytic fast pyrolysis using Johnson Matthey catalyst .

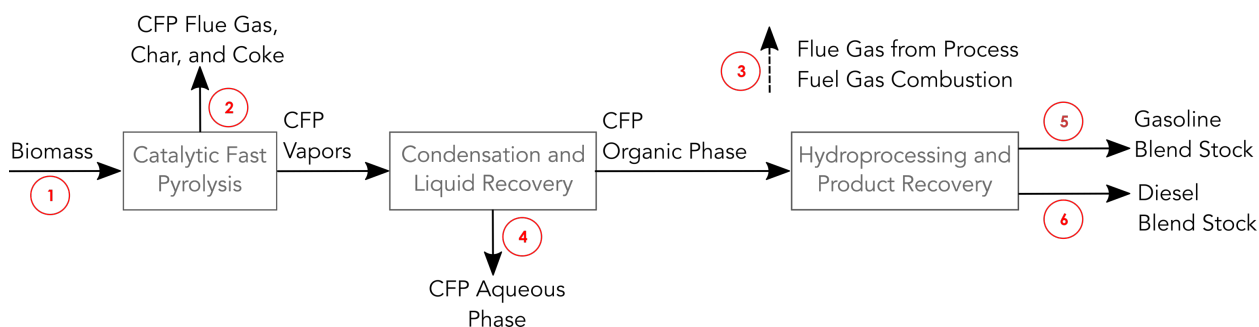
Sample	Carbon %	Hydrogen %	Nitrogen %	Oxygen%
Aqueous Phase As Received	3	11	<1%	86
Aqueous Phase on a Karl Fischer Moisture Free Basis	38	4	<1%	58

**Table S2:** Estimated carbon balance for CFP process with varying aqueous carbon content.

Cases with Carbon in Aqueous Phase:	Stream	1.3%†	3%*	14%*
Biomass	(1)	100.0%	100.0%	100.0%
CFP Flue Gases	(2)	31.4%	31.4%	31.4%
Process Fuel Gas	(3)	25.7%	25.7%	25.7%
Aqueous Phase	(4)	1.3%	3%	14%
Gasoline Blendstock	(5)	18.6%	17.9%	12.9%
Diesel Blendstock	(6)	22.9%	22.0%	15.9%

†Based on design report (NREL/TP-5100-62455) *ex situ* case with low aqueous carbon<sup>1</sup>

\*Estimated by diverting carbon from gasoline & diesel fuel blendstocks in 1.3% case



**Fig. S1:** Process flow diagram for overall carbon balance.

**Table S3:** Summary analysis of CFP LLE Operation

Stream		CFP Aqueous	Concentrated Organics
Solvent %		97 (Water)	43 (EtOAc)
CFP Product %		3	57
CFP Product Distribution	Phenolics	4.6	14.1
	Catecholics	6.3	21.2
	Phenol	6.3	15.6
	Ketones	6.2	3.2
	Catechol	15.8	31.6
	Other	14.8	2.7
	Acids	46.0	11.6

#### Materials and methods for detailed chemical composition of *ex situ* CFP aqueous streams

All analyses were performed in triplicate independent experiments unless otherwise indicated. Water content was measured using Karl Fisher titration according to the standard ASTM E203-08, using a Metrome 701 Titrino titration system using methanol as a solvent and Hydranal®-Composite 5 reagent (Sigma Aldrich, St. Louis, MO) as the titrant. Total organic carbon (TOC) was measured via a combustion catalytic oxidation method after sample acidification by concentrated hydrochloric acid using a Shimadzu TOC-L<sub>CSH</sub> analyzer (Shimadzu, Columbia, MD). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed following a concentrated nitric acid digestion of samples. Inorganic species were measured using a Spectro Arcos ICP analyzer monitoring emission lines in the range of 130 to 773 nm (Spectro Analytical Instruments Inc., Kleve, Germany). The instrument was calibrated with commercial standards and samples were run in nine independent measurements (n=9).

#### Liquid chromatography quantitative analysis

Infusion-tandem mass analysis was performed for initial identification of water-soluble analytes in previous work<sup>2</sup>, and identifications remained effective for the current parameter dependent *ex situ* CFP aqueous samples. Authentic standards were obtained in the highest purity available and used for analyte identity confirmation and quantitation. LC quantitative analysis was performed in triplicate independent experiments (n=3) and all quantitative standard curves were maintained with an R<sup>2</sup> value of  $\geq 0.995$  with five or more points of reference ranging between concentrations of 1 to 100  $\mu\text{g mL}^{-1}$  for mass spectrometry experiments and 0.05 to 20  $\text{mg mL}^{-1}$  for RID. Additionally, if necessary, samples were diluted with methanol accordingly to fit within the linear regions of the calibration curves. All analytes were analyzed by more than one method for confirmation of quantitation accuracy.

Organic acids, select aldehydes, and select aldehydes were quantified via an Agilent 1100 HPLC system fitted in-line with a diode array (DAD) and a RID (Agilent Technologies, Santa Clara, CA). Analytes were separated using an Aminex HPX-87H 9  $\mu\text{m}$ , 7.8 mm i.d.  $\times$  300 mm column (Bio-Rad Laboratories, Hercules, CA) using an isocratic mobile phase of 5 mM H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.6  $\text{mL min}^{-1}$ . Column and RID detector temperatures were maintained at 55°C.

The main method of analysis for phenolic, aromatic, nitrogen-containing and larger molecular mass ketone compounds was performed on an Agilent 1100 HPLC system equipped with a DAD and an Ion Trap SL (Agilent Technologies, Santa Clara, CA) MS with in-line ESI. Each sample was injected at a volume of 25  $\mu\text{L}$  into the LC/MS system. Compounds were separated using a Develosil C30 RPaqueous, 5 $\mu\text{m}$ , 4.6  $\times$  250 mm column (Phenomenex, Torrance, CA) at an oven temperature of 30°C. The chromatographic eluents consisted of A) water modified with 0.03% formic acid, and B) acetonitrile/water (9:1, v/v) also modified with 0.03% formic acid. At a flow rate of 0.7  $\text{mL min}^{-1}$ , the eluent gradient was as follows: 0-3 min, 0% B; 16 min, 7% B; 21 min, 8.5% B; 34 min, 10% B; 46 min, 25% B; 51-54 min, 30% B; 61 min, 50% B; and lastly 64-75 min, 100% B before equilibrium. Flow from the HPLC-DAD was directly routed in series to the ESI-MS ion trap. The DAD was used to monitor chromatography at 210 and 264 nm for a direct comparison to MS data. MS and MS/MS parameters are as follows: smart parameter setting with target mass set to 165 Da, compound stability 70%, trap drive 50%, capillary at 3500 V, fragmentation amplitude of 0.75 V with a 30 to 200 % ramped voltage implemented for 50 msec, and an isolation width of  $m/z$  2 (He collision gas). The ESI nebulizer gas was set to 60 psi, with dry gas flow of 11  $\text{L min}^{-1}$  held at 350°C. Into each sample and standard mixture, 0.01  $\text{g L}^{-1}$  3,4-dihydroxybenzaldehyde (97% purity, Sigma Aldrich, St. Louis, MO) was added to adjust for chromatographic shift and detector response. MS scans and precursor isolation-fragmentation scans were

performed across the range of 40-750 Da. LC-DAD/MS was also used to confirm the quantitation of many organic acids and aldehydes.

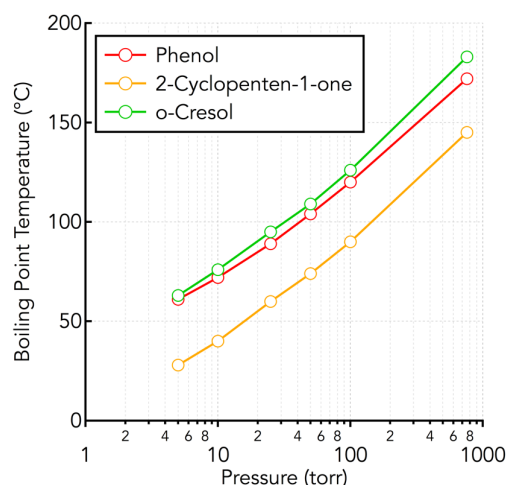
#### **Gas chromatography quantitative analysis**

GC-MS was the primary analysis for select ketone, aldehyde, and alcohol compounds. An Agilent 6890N gas chromatograph and Agilent 5973N mass-selective detector (Agilent Technologies, Santa Clara, CA) was used for the identification of analytes. Using a splitless injection, 1  $\mu\text{L}$  sample volume was introduced onto a 30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness Stabilwax column (Restek Corp., Bellefonte, PA) at 260°C. The helium flow was kept constant at 1 ml  $\text{min}^{-1}$  with an oven program as follows: the initial column temperature of 35°C was held for 3 min and then increased to 225°C at 5°C  $\text{min}^{-1}$  with a hold time of 1 min, and lastly, to 250°C at 15°C  $\text{min}^{-1}$  with a hold time of 5 min. Alternatively, a 30 m  $\times$  0.25 mm i.d., 1  $\mu\text{m}$  film thickness HP-1MS column was used (Agilent, Santa Clara, CA) with the following oven program: the initial column temperatures of 32°C was held for 5 min and then increased to 225°C at 6°C  $\text{min}^{-1}$  with a hold time of 1 min, and finally, to 300°C at 10.3°C  $\text{min}^{-1}$  with a hold time of 1 min. Electron impact ionization was used at 70 eV electron energy and a mass scan range of  $m/z$  25 – 450. An internal standard of 1,2-diphenylbenzene (99.9+% purity, AccuStandard, New Haven, CT) was added to all standards and samples at a concentration of 0.05 g  $\text{L}^{-1}$  to adjust for any detector response shift. An Agilent Environmental ChemStation G1701DA version D.00.00.38 and NIST 2011 library was used for data analysis. All gas chromatography quantitative analysis was performed in triplicate independent experiments ( $n=3$ ) and all quantitative standard curves ranged between 1 to 100  $\mu\text{g mL}^{-1}$  with no less than four points of reference and were maintained with a correlation  $R^2$  value of  $\geq 0.995$ . Additionally, GC-MS was used to confirm the quantitation of many aldehydes, organic acids and aromatic compounds from LC analysis. Authentic standards were obtained for quantitation in the highest purity available as listed in **Table S4**.

**Table S4:** Chemical characterization of ex situ CFP aqueous streams presented in g kg<sup>-1</sup> on a wet weight basis

Compound	Mixed Hardwood Feedstock	Pine Feedstock	
	JM Catalyst A	JM Catalyst A	JM Catalyst B
Acetic acid	5.45	4.14	3.36
Formic acid	0.59	0.98	0.73
Propanoic acid	0.07	0.10	0.08
2-Methylidenebutanedioic acid	0.38	0.65	0.55
2-Hydroxyacetic acid	0.26	0.43	0.03
Acetaldehyde	0.34	0.51	0.21
2-Hydroxyacetaldehyde	0.09	0.16	ND
Formaldehyde	0.81	1.07	1.01
Furan-2-carbaldehyde	1.83	1.39	1.47
Propan-2-one	2.03	2.06	2.01
But-3-en-2-one	ND	0.09	ND
Butane-2,3-dione	0.09	0.12	0.05
Cyclopentanone	0.02	0.02	0.02
Cyclopent-2-en-1-one	0.22	0.19	0.16
2-Methylcyclopent-2-en-1-one	0.02	0.02	0.02
2,3-Dimethylcyclopent-2-en-1-one	0.02	0.02	0.01
3-Methylcyclopentane-1,2-dione	0.03	0.03	0.02
2-Hydroxy-3-methylcyclopent-2-en-1-one	0.04	0.04	0.04
Phenol	2.24	2.94	3.43
2-Methylphenol	0.81	0.92	1.07
3-Methylphenol	1.82	2.14	2.46
4-Methylphenol	0.68	0.72	0.88
2,3-Dimethylphenol	T	0.02	0.03
2,5-Dimethylphenol	0.63	0.75	0.83
2,6-Dimethylphenol	0.02	0.02	0.02
3,4-Dimethylphenol	T	0.01	0.01
3,5-Dimethylphenol	0.09	0.04	0.05
2,3,5-Trimethylphenol	0.02	0.01	0.01
2-Methoxyphenol	0.01	0.01	0.01
2,6-Dimethoxyphenol	T	0.24	T
2-Ethylphenol	0.18	0.28	0.31
3-Ethylphenol	0.01	0.03	0.04
Benzene-1,2-diol	0.28	4.57	3.57
Benzene-1,4-diol	0.44	0.70	0.55
2-Methylbenzene-1,4-diol	0.25	0.22	0.21
3-Methylbenzene-1,2-diol	1.06	1.14	0.85
4-Methylbenzene-1,2-diol	0.81	0.96	0.70
2,5-Dimethylbenzene-1,4-diol	0.45	0.29	0.31
4,5-Dimethylbenzene-1,3-diol	0.10	0.09	0.09
3-Ethylbenzene-1,2-diol	0.11	0.10	0.10
4-Ethylbenzene-1,2-diol	0.47	0.46	0.50
4-Ethylbenzene-1,3-diol	0.35	0.33	0.40
4-Hydroxybenzoic acid	0.04	ND	ND
4-Hydroxy-3-methoxybenzoic acid	0.21	0.12	0.10
2-(4-hydroxy-3-methoxyphenyl)acetic acid	0.21	0.12	0.10
3,4-Dihydroxybenzaldehyde	0.01	0.01	T
4-Hydroxy-3-methoxybenzaldehyde	0.04	0.04	0.04
Methanol	1.43	1.14	0.87
Propan-1-ol	0.28	0.25	0.21
Butan-1-ol	0.37	0.29	0.26
Naphthalen-1-ol	0.04	0.03	0.04
Naphthalen-2-ol	0.03	0.04	0.05

T = trace amounts detected, < 0.01 g kg<sup>-1</sup>; ND = not detected in the sample, below the limit of detection



**Figure S2:** Boiling point as measured on distillation column under infinite reflux as a function of pressure.

### Complexities of Distilling Concentrated Organics

**Nonideal Interactions:** Distillation of a binary system of phenol and 2-cyclopenten-1-one produced an azeotrope at the atmospheric equivalent temperature of  $194^{\circ}\text{C}_{\text{AET}}$  ( $126^{\circ}\text{C}$  at 100 torr) and  $x_{\text{Phenol}}=0.66$ , which is previously unreported in the literature. The result of this deviation is the presence of 2-cyclopenten-1-one, with a pure component boiling point of  $150^{\circ}\text{C}$ , in fraction F4 which is collected between  $189 - 229^{\circ}\text{C}_{\text{AET}}$  ( $103 - 138^{\circ}\text{C}$  at 50 torr).

**Species Generating Reaction:** Acetic acid unexpectedly appears in fraction F3. It has a boiling point of  $118^{\circ}\text{C}$  while fraction F3 was collected between  $160$  and  $189^{\circ}\text{C}_{\text{AET}}$  ( $78 - 103^{\circ}\text{C}$  at 50 torr). It is unlikely that the presence of acetic acid is due to thermodynamic interactions, as no azeotrope between acetic acid and phenolic compounds has been reported to our knowledge and mass balance closure around acetic acid indicates a  $29\pm 1\%$  mass increase relative to the amount charged to the boiler. The increase in the amount of acetic acid along with its presence in fraction F3 suggests its generation during distillation of fraction F3. Generation of another compound, propionic acid, is also observed. The compound is detected in fraction F3, which is unexpected as its boiling point is  $141^{\circ}\text{C}$ . The reaction(s) generating propionic acid and acetic were not observed in the distillation of a model mixture of acetic acid, 2-cyclopenten-1-one, phenol, *o*-cresol, *p*-cresol, and catechol.

**Table S5:** Summary analysis of distillate fractions

Unit Operation Stream	Distillation of Concentrated Organics						Phenol Purification		
	F1	F2	F3	F4	F5	F6	F3.1	F3.2	F3.3
Ethyl Acetate	100.0	20.6	0.6	0.0	0.0	0.0	0.0	0.0	0.0
Phenolics	0.0	0.0	9.7	55.8	3.8	1.4	0.0	2.7	5.7
Catecholics	0.0	0.0	0.0	0.8	16.6	40.2	0.0	0.0	0.0
Phenol	0.0	0.0	63.6	28.6	0.3	0.0	0.4	77.2	91.7
Ketones	0.0	0.0	0.6	8.2	1.3	0.0	0.0	1.0	0.5
Catechol	0.0	0.0	0.0	5.5	76.4	57.2	1.4	0.9	0.0
Other	0.0	0.0	1.3	0.1	1.6	1.2	0.1	1.0	0.8
Acids	0.0	79.4	24.2	1.0	0.0	0.0	98.1	17.2	1.3

**Table S6: Variable Operating Costs**

<b>Variable Operating Costs</b>	<b>Annual Cost</b>	<b>Cost Per kg Product (cents)</b>
Ethyl Acetate Makeup (at \$0.65/lb) <sup>1</sup>	\$862,760	28.01
Electricity (at \$0.068/kWh) <sup>2</sup>	\$13,368	0.43
200 psig Steam (at \$4.42/1000 lb) <sup>3</sup>	\$309,665	10.05
Cooling Water (at \$0.09/ 1000 gallon) <sup>4</sup>	\$896	0.03
<b>Total Variable Operating Costs</b>	<b>\$1,186,689</b>	<b>38.53</b>
<b>Fixed Operating Costs</b>		
Salaries	\$581,803	18.89
Overhead and Benefits	\$523,622	17.00
Maintenance	\$153,273	4.98
Insurance and Taxes	\$35,764	1.16
<b>Total Fixed Operating Costs</b>	<b>\$1,294,462</b>	<b>42.03</b>
<b>Total Operating Costs</b>	<b>\$2,481,151</b>	<b>80.56</b>
<b>Minimum Product Selling Price (MPSP)</b>		<b>106.28</b>
Average Capital Charge (MPSP minus operating costs)		25.72

**Table S7: Steam requirements for distillation columns and other unit operations.**

<b>Unit Operation</b>	<b>200 psig stm (%)</b>	<b>200 psig stm (lb/hr)</b>
Distillation Column 1	30%	1198
Distillation Column 2	67%	2702
Other	3%	126
<b>Total</b>	<b>100%</b>	<b>4026</b>

**Table S8: Typical Phenol Purity Specifications**

<b>Quality Metric</b>	<b>High-purity phenol</b>	<b>Ultrahigh-purity Phenol</b>
Color, (APHA) <sup>3,4</sup>	5	5
Water (wt% ppm) <sup>3</sup>	300	300
Solidification point (°C) <sup>3,5</sup>	40.8	40.8
Total carbonyls (wt% ppm) <sup>3,5</sup>	30	15
Total GC impurities (wt% ppm) <sup>3</sup>	100	30
Cresols (wt% ppm) <sup>3</sup>	50	25
2-Methylbenzofuran (wt% ppm) <sup>3</sup>	5	1
Purity (wt%) <sup>6</sup>	99.96	99.99
Iron (wt% ppm) <sup>5</sup>	0.5	-
α-Methylstyrene (wt% ppm) <sup>6</sup>	100	10
Hydroxyacetone (wt% ppm) <sup>5</sup>	20	-

**Table S9:** Composition and Flow Rates of Streams in TEA Model

Component	Experimental Concentrations of Aqueous Phase (g/kg)	Modeled Flowrate	
		Aqueous (kg/h)	Product (kg/h)
<i>Phenolics (with at least 1 phenolic group†)</i>	17.35	550.887	359.385
Total	1000	31751.440	390.637
<i>Ethyl Acetate (solvent)</i>	N/A	N/A	0.495
<i>Water</i>	968.95	30,765.558	0.000
Formaldehyde	1.07	33.974	0.000
Formic acid	0.98	31.116	0.069
Methanol	1.14	36.197	0.000
Acetaldehyde	0.51	16.193	0.000
Acetic acid	4.14	131.451	0.890
2-Hydroxyacetaldehyde	0.16	5.080	0.103
2-Hydroxyacetic acid	0.43	13.653	0.129
Propan-2-one	2.06	65.408	0.000
Propanoic acid	0.1	3.175	0.415
Propan-1-ol	0.25	7.938	0.008
But-3-en-2-one	0.09	2.858	0.002
Butane-2,3-dione	0.12	3.810	0.006
Butan-1-ol	0.29	9.208	3.616
Furan-2-carbaldehyde	1.39	44.135	21.317
Cyclopent-2-en-1-one	0.19	6.033	1.554
2-Methylidenebutanedioic acid	0.65	20.638	0.881
Cyclopentanone	0.02	0.635	0.239
Phenol†	2.94	93.349	71.533
Benzene-1,2-diol†	4.57	145.104	61.156
Benzene-1,4-diol†	0.7	22.226	9.367
2-Methylcyclopent-2-en-1-one	0.02	0.635	0.404
3-Methylcyclopentane-1,2-dione	0.03	0.953	0.345
2-Hydroxy-3-methylcyclopent-2-en-1-one	0.04	1.270	0.155
3,4-Dihydroxybenzaldehyde†	0.01	0.318	0.057
2-Methylphenol†	0.92	29.211	25.994
3-Methylphenol†	2.14	67.948	60.333
4-Methylphenol†	0.72	22.861	20.296
2-Methoxyphenol†	0.01	0.318	0.277
3-Methylbenzene-1,2-diol†	1.14	36.197	12.584
4-Methylbenzene-1,2-diol†	0.96	30.481	19.421
2-Methylbenzene-1,4-diol†	0.22	6.985	4.451
2,3-Dimethylcyclopent-2-en-1-one	0.02	0.635	0.623
4-Hydroxy-3-methoxybenzaldehyde†	0.04	1.270	1.043
4-Hydroxy-3-methoxybenzoic acid†	0.12	3.810	2.555
2,3-Dimethylphenol†	0.02	0.635	0.604
2,5-Dimethylphenol†	0.75	23.814	22.670
2,6-Dimethylphenol†	0.02	0.635	0.606
3,4-Dimethylphenol†	0.01	0.318	0.302
3,5-Dimethylphenol†	0.04	1.270	1.207
2-Ethylphenol†	0.28	8.890	8.514
3-Ethylphenol†	0.03	0.953	0.911
2,5-Dimethylbenzene-1,4-diol†	0.29	9.208	7.450
4,5-Dimethylbenzene-1,3-diol†	0.09	2.858	2.312
3-Ethylbenzene-1,2-diol†	0.1	3.175	1.891
4-Ethylbenzene-1,2-diol†	0.46	14.606	8.697
4-Ethylbenzene-1,3-diol†	0.33	10.478	6.239
2,6-Dimethoxyphenol†	0.24	7.620	4.881
2-(4-hydroxy-3-methoxyphenyl) acetic acid†	0.12	3.810	2.455
2,3,5-Trimethylphenol†	0.01	0.318	0.311
Naphthalen-1-ol†	0.03	0.953	0.544
Naphthalen-2-ol†	0.04	1.270	0.723

**Table S10:** Capital Costs for the Project in 2014 dollars for the base case

<b>Capital Costs</b>	<b>Amount</b>
Total Installed Capital	\$2,694,678
Other Direct Costs	\$498,515
Indirect Costs	\$1,915,916
<b>Fixed Capital Investment (excluding land)</b>	<b>\$5,109,109</b>
Working Capital	\$255,455
Land	\$140,000

<sup>1</sup> Inferred from information (57.50-58.50 cents/lb ) by Platts at <https://www.platts.com/latest-news/petrochemicals/houston/three-us-producers-raise-ethyl-acetate-prices-21625451> (accessed Feb 17, 2018) and other proprietary sources.

<sup>2</sup> Inferred from Energy Information Administration (EIA) November 2017 industrial information at <https://www.eia.gov/electricity/data/browser/#/topic/7?agg=2,0,1&geo=g&freq=M> (accessed Feb 17, 2018)

<sup>3</sup> Calculated using methods in "How to Calculate the True Cost of Steam by US DOE EERE, DOE/GO-102003-1736, Sept 2003" and a 5-year average (2013-2017) natural gas price of \$3.25/MMBtu from EIA (<https://www.eia.gov/dnav/ng/hist/rngwhhdm.htm> accessed Feb 17, 2018)

<sup>4</sup> Cost of \$0.05/1000 gallon in year 2000 dollars from Product and Process Design Principles: Synthesis, Analysis, and Evaluation, 2nd Edition by Seider, W.D.; Seader, J.D.; Lewin, D.R. John Wiley and Sons, 2004. escalated to \$0.09/1000 gallons in 2014 dollars using the US Producer Price Index for chemical manufacturing

### Cost Sensitivities

A 20% increase in the ethyl acetate unit cost results in a 5.4% increase in the MPSP. A 20% increase in steam cost increases the MPSP by 1.9%, while other utilities – electricity and cooling water – have negligible impacts. Fixed operating costs associated with personnel (**Table S5**) were based on sharing some of the functions with the main CFP plant. This cost can go up for standalone operations and go down with further sharing of job functions with the CFP plant; a 20% increase in salaries and overhead can increase the MPSP by 6.9%.

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