Supplementary Information

Valorization of Aqueous Waste Streams from Thermochemical Biorefineries

A. Nolan Wilson¹, Abhijit Dutta¹, Brenna A. Black², Calvin Mukarakate¹, Kim Magrini¹, Joshua A. Schaidle¹, William E. Michener², Gregg T. Beckham¹, Mark R. Nimlos¹,³

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 carbon¹
*Estimated by diverting carbon from gasoline & diesel fuel blendstocks in 1.3% case

Fig. S1: Process flow diagram for overall carbon balance.
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 Hydralan®-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>C</sub>SH 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, 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 ≥ 0.995 with five or more points of reference ranging between concentrations of 1 to 100 µg mL<sup>-1</sup> for mass spectrometry experiments and 0.05 to 20 mg mL<sup>-1</sup> 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 µm, 7.8 mm i.d. x 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 mL min<sup>-1</sup>. 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 µL into the LC/MS system. Compounds were separated using a Develosil C30 RPaqueous, 5µm, 4.6 x 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 mL min<sup>-1</sup>, 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 L min<sup>-1</sup> held at 350°C. Into each sample and standard mixture, 0.01 g L<sup>-1</sup> 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

Table S3: Summary analysis of CFP LLE Operation

| Stream          | CFP Aqueous | Concentrated Organics |
|-----------------|-------------|-----------------------|
| CFP Product %   | Solvent %   |                       |
| Phenolics       | 4.6         | 14.1                  |
| Catecholics     | 6.3         | 21.2                  |
| Phenol          | 6.3         | 15.6                  |
| Ketones         | 6.2         | 3.2                   |
| Catecholic      | 15.8        | 31.6                  |
| Other           | 14.8        | 2.7                   |
| Acids           | 46.0        | 11.6                  |
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 µL sample volume was introduced onto a 30 m × 0.25 mm i.d., 0.25 µm film thickness Stabilwax column (Restek Corp., Bellefonte, PA) at 260°C. The helium flow was kept constant at 1 ml 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 min⁻¹ with a hold time of 1 min, and lastly, to 250°C at 15°C min⁻¹ with a hold time of 5 min. Alternatively, a 30 m × 0.25 mm i.d., 1 µm 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 min⁻¹ with a hold time of 1 min, and finally, to 300°C at 10.3°C 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 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 µg mL⁻¹ with no less than four points of reference and were maintained with a correlation R² value of ≥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\(^{-1}\) 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-Methyldenebutanedioic acid    | 0.38                     | 0.65          | 0.55          |
| 2-Hydroxyacetic acid            | 0.26                     | 0.43          | 0.03          |
| Acetaldehyde                    | 0.34                     | 0.51          | 0.21          |
| 2-Hydroxycetaldehyde            | 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\(^{-1}\); ND = not detected in the sample, below the limit of detection.
Complexities of Distilling Concentrated Organics

Nonideal Interactions: Distillation of a binary system of phenol and 2-cyclopent-1-one produced an azeotrope at the atmospheric equivalent temperature of 194°C\(_{\text{AET}}\) (126°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-cyclopent-1-one, with a pure component boiling point of 150°C, in fraction F4 which is collected between 189 – 229°C\(_{\text{AET}}\) (103 – 138°C at 50 torr).

Species Generating Reaction: Acetic acid unexpectedly appears in fraction F3. It has a boiling point of 118°C while fraction F3 was collected between 160 and 189°C\(_{\text{AET}}\) (78 – 103°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±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°C. The reaction(s) generating propionic acid and acetic were not observed in the distillation of a model mixture of acetic acid, 2-cyclopent-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 |
| Catechol             |        | 0.0 | 0.0 | 0.0 | 0.8 | 16.6 | 40.2 | 0.4 | 77.2 | 91.7 |
| Phenol               |        | 0.0 | 0.0 | 63.6 | 28.6 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 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

| Variable Operating Costs                  | Annual Cost  | Cost Per kg Product (cents) |
|------------------------------------------|--------------|-----------------------------|
| Ethyl Acetate Makeup (at $0.65/lb)¹      | $862,760     | 28.01                       |
| Electricity (at $0.068/kWh)²             | $13,368      | 0.43                        |
| 200 psig Steam (at $4.42/1000 lb)³      | $309,665     | 10.05                       |
| Cooling Water (at $0.09/ 1000 gallon)⁴  | $896         | 0.03                        |
| **Total Variable Operating Costs**       | **$1,186,689** | **38.53**                  |

### Fixed Operating Costs

|                      |               |                |
|----------------------|---------------|----------------|
| Salaries             | $581,803      | 18.89          |
| Overhead and Benefits| $523,622      | 17.00          |
| Maintenance          | $153,273      | 4.98           |
| Insurance and Taxes  | $35,764       | 1.16           |
| **Total Fixed Operating Costs**        | **$1,294,462** | **42.03**      |

### Total Operating Costs

|                      |               |                |
|----------------------|---------------|----------------|
|                      | **$2,481,151** | **80.56**      |

**Minimum Product Selling Price (MPSP)**

106.28

**Average Capital Charge (MPSP minus operating costs)**

25.72

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

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

### Table S8: Typical Phenol Purity Specifications

| Quality Metric                  | High-purity phenol | Ultrahigh-purity Phenol |
|--------------------------------|--------------------|-------------------------|
| Color, (APHA)³,⁴               | 5                  | 5                       |
| Water (wt% ppm)³               | 300                | 300                     |
| Solidification point (°C)³,⁵   | 40.8               | 40.8                    |
| Total carbonyls (wt% ppm)³,⁵   | 30                 | 15                      |
| Total GC impurities (wt% ppm)³ | 100                | 30                      |
| Cresols (wt% ppm)³             | 50                 | 25                      |
| 2-Methylbenzofuran (wt% ppm)³ | 5                  | 1                       |
| Purity (wt%)⁶                  | 99.96              | 99.99                   |
| Iron (wt% ppm)⁵                | 0.5                | -                       |
| α-Methylstyrene (wt% ppm)⁶     | 100                | 10                      |
| Hydroxyacetone (wt% ppm)⁵      | 20                 | -                       |
| Component | Experimental Concentrations of Aqueous Phase (g/kg) | Modeled Flowrate (kg/h) |
|-----------|---------------------------------------------------|------------------------|
| **Phenolics** | | |
| Phenolics (with at least 1 phenolic group†) | 17.35 | 550.887 | 359.385 |
| Total | 1000 | 3175.440 | 390.637 |
| Ethyl Acetate (solvent) | N/A | N/A | 0.495 |
| Water | 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-Hydroxyacetaldelyde | 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-Methyldibutane dioic 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-Methylicyclopent-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-Methybenzene-1,2-diol† | 1.14 | 36.197 | 12.584 |
| 4-Methybenzene-1,2-diol† | 0.96 | 30.481 | 19.421 |
| 2-Methybenzene-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-methoxybenaldehyde† | 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-Dimethylphenol† | 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

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

1 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.

2 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)

3 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)

4 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%.

1 A. Dutta, A. Sahir, E. Tan, D. Humbird, L. J. Snowden-swan, P. Meyer, J. Ross, D. Sexton, R. Yap, J. Lukas, A. Dutta, A. Sahir, E. Tan, D. Humbird, L. J. Snowden-swan, P. Meyer, J. Ross, D. Sexton, R. Yap, and J. Lukas, *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels*, 2015.

2 B. A. Black, W. E. Michener, K. J. Ramirez, M. J. Biddy, B. C. Knott, M. W. Jarvis, J. Olstad, O. D. Mante, D. C. Dayton and G. T. Beckham, *ACS Sustain. Chem. Eng.*, 2016, 4, 6815–6827.

3 R. J. Schmidt, in *Handbook of Petrochemical Production Processes*, McGraw-Hill Education.

4 A. Moore and R. Birkhoff, in *Handbook of Petrochemical Production Processes*, 2005.

5 E. Fraini, D. West and G. Mignin, in *Handbook of Petrochemical Production Processes*, 2005.

6 R. A. Meyers, in *Handbook of Petrochemicals Production Processes*, 2005.