Additional Files

**Integrated experimental and technoeconomic evaluation of two-stage Cu-catalyzed alkaline-oxidative pretreatment of hybrid poplar**

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Table S1. Raw material prices considered in the technoeconomic analysis.

|  |  |  |
| --- | --- | --- |
| **Raw Material** | **2011 Price  $/U.S. ton** | **References** |
| Sulfuric Acid, 93% | 99.8 | [1] |
| Corn Steep Liquor | 63 | [2] |
| Diammonium Phosphate | 1,097 | [2] |
| Sorbitol | 1,253 | [2] |
| Glucose | 645 | [2] |
| Host nutrients | 913 | [2] |
| Sulfur Dioxide | 338 | [2] |
| Boiler Chemicals | 5,557 | [2] |
| Lime | 222 | [2] |
| Natural Gas | 227 | [2] |
| Cooling Tower Chemicals | 3,330 | [2] |
| Electricity ($/kWh) | 0.0572 | [2] |
| Makeup Water | 0.29 | [2] |
| Caustic (As pure) | 166 | [3] |
| Feedstock (poplar, dry basis) | 60 | [4] |
| Hydrogen Peroxide (50%) | 363 | [5] |
| Copper Sulfate | 27 | [6] |
| BPY (2,2'-Bipyridine) | 53,520 | [7] |

Table S2. Operating conditions considered for technoeconomic assessment of industrial scale bioethanol plant utilizing two stage Cu-AHP preteatments. The first three columns use data that were collected during this investigation. Entries in the fourth column, for the best-case, assume that glucose and xylose yields from the “120 °C NaOH-H2O PE + Cu-AHP case” remain unchanged when hydrogen peroxide, 2,2ʹ-bipyridine (bpy), and enzyme loadings are reduced.

|  | 30 °C NaOH-H2O PE + Cu-AHP | | | 120 °C NaOH-H2O PE + Cu-AHP | | 120 °C NaOH-EtOH PE + Cu-AHP | | Hypothetical-case as identified by sensitivity analysis | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **1st stage pre-extraction** |  | | | | | | | |
| Temperature (ᵒC) | 30 °C | | | 120 °C | | 120 °C | | 120 °C | |
| NaOH (g/g dry biomass) | 0.1 | | | 0.1 | | 0.1 | | 0.1 | |
| Solids loadinga | 30% | | | 30% | | 30% | | 30% | |
| Dissolved xylanb | 5% | | | 27% | | 20% | | 27% | |
| Dissolved celluloseb | 1% | | | 4% | | 2 | | 4% | |
| Dissolved ligninb | 5% | | | 28% | | 19% | | 28% | |
| Residence time | 1 (hr) | | | 1 (hr) | | 1 (hr) | | 1 (hr) | |
| **2nd stage pretreatment** |  | | | | | | | |
| Temperature | 30 °C | | | 30 °C | | 30 °C | | 30 °C | |
| NaOH (g/g dry biomass) | 0.1 | | | 0.1 | | 0.1 | | 0.1 | |
| H2O2 (g/g dry biomass) | 0.1 | | | 0.1 | | 0.1 | | 0.06 | |
| CuSO4 (mM) | 1 | | | 1 | | 1 | | 1 | |
| bpy (mM) | 2 | | | 2 | | 2 | | 1 | |
| Dissolved xylanc | 37% | | | 25% | | 25% | | 25% | |
| Dissolved cellulose c | 5% | | | 1% | | 3% | | 1% | |
| Dissolved lignin c | 53% | | | 70% | | 68% | | 70% | |
| Residence time | 23 (hr) | | | 23 (hr) | | 23 (hr) | | 23 (hr) | |
| Solids loading\* | 30% | | | 30% | | 30% | | 30% | |
| **Net lignin removal** d | **55%** | | | **78%** | | **74%** | | **78%** | |
| **Enzymatic hydrolysis** |  | |  | |  | |  | |
| Glucose yield | 96% | | | 93% | | 93% | | 93% | |
| Xylose yield | 94% | | | 98% | | 97% | | 98% | |
| Time (hr) | 72 | | | 72 | | 72 | | 72 | |
| Enzyme loading (mg protein/g glucan) | 60 | | | 30 | | 30 | | 20 | |
| Solids loadinga | 20% | | | 20% | | 20% | | 20% | |
| Temperature (ᵒC) | 50 | | | 50 | | 50 | | 50 | |
| **Fermentation** |  | | |  | |  | |  | |
| Temperature (ᵒC)a | 32 | | | 32 | | 32 | | 32 | |
| Time (hr)a | 36 | | | 36 | | 36 | | 36 | |
| Glucose to EtOH conversion | | 95% | | 95% | | 95% | | 95% | |
| Xylose to EtOH conversion | 85% | | | 85% | | 85% | | 85% | |

a Assumed based on NREL report ‎[1].

b Grams dissolved constituent/grams constituent in original biomass.

c Grams dissolved constituent/grams constituent in pre-extracted biomass.

d The net lignin dissolved cannot be directly computed by addition of the 1st stage pre-extraction and 2nd stage pretreatment because the basis units differ.

Table S3. Comparison of raw material costs (MM $/year) for 60 MM gal/year bioethanol plant utilizing two-stage Cu-AHP pretreatments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Process Area | 30 °C NaOH-H2O PE + Cu-AHP  MM$/year | 120 °C NaOH-H2O PE + Cu-AHP  MM$/year | 120 °C NaOH-EtOH PE + Cu-AHP  MM$/year | Hypothetical-case  as identified by sensitivity analysis  MM$/year |
| Area 100: Feedstock handling |  |  |  |  |
| Feedstock | 40.22 | 44.46 | 43.17 | 44.45 |
| Area 200: Pretreatment |  |  |  |  |
| Sulfuric acid, 93% | 8.17 | 7.85 | 8.01 | 7.84 |
| Sodium hydroxide | 21.49 | 22.31 | 22.07 | 22.31 |
| Hydrogen peroxide | 45.08 | 43.27 | 44.16 | 25.95 |
| Copper sulfate | 0.01 | 0.01 | 0.01 | 0.01 |
| Bipyridine | 29.51 | 28.34 | 28.95 | 13.70 |
| Area 300: Enzymatic Hydrolysis & Fermentation |  |  |  |  |
| Corn steep liquor | 0.63 | 0.63 | 0.58 | 0.60 |
| Diammonium phosphate | 1.37 | 1.36 | 1.26 | 1.31 |
| Sorbitol | 0.47 | 0.47 | 0.43 | 0.45 |
| Area 400: Enzyme Production |  |  |  |  |
| Glucose | 48.23 | 27.07 | 26.11 | 18.04 |
| Corn steep liquor | 0.32 | 0.18 | 0.17 | 0.12 |
| Ammonia | 1.77 | 1.00 | 0.96 | 0.66 |
| Host nutrients | 1.90 | 1.07 | 1.03 | 0.71 |
| Sulfur dioxide | 0.17 | 0.10 | 0.09 | 0.06 |
| Area 800: Boiler and Turbogenerator |  |  |  |  |
| Boiler chemicals | 0.0023 | 0.01 | 0.0029 | 0.01 |
| Lime | 0.20 | 0.13 | 0.12 | 0.10 |
| Natural gas | − | − | 1.84 | 0.00 |
| Disposal of ash | 0.33 | 0.13 | 0.12 | 0.12 |
| Area 900: Utilities |  |  |  |  |
| Cooling tower chemicals | 0.09 | 0.06 | 0.04 | 0.05 |
| Makeup water | 0.42 | 0.45 | 0.36 | 0.41 |
| Purchased electricity from the grid | − | − | 12.34 | − |
| By-Product Revenue |  |  |  |  |
| Electricity sold to the grid | −2.82 | −3.63 | − | −5.21 |
| **Total Raw Materials Cost (MM $/year)** | **197.6** | **175.3** | **191.8** | **131.7** |
| **Fixed Operating Costs (MM $/year)** | **15.5** | **12.6** | **12.7** | **12.1** |
| **Total Operating Cost (MM $/year)** | **213.1** | **187.9** | **204.5** | **143.8** |

Table S4. Total capital investments of 60 MM gal/year bioethanol plant utilizing two-stage Cu-AHP pretreatments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Process Area** | 30 °C NaOH-H2O PE + Cu-AHP  MM $ | 120 °C NaOH-H2O PE + Cu-AHP  MM $ | 120 °C NaOH-EtOH PE + Cu-AHP  MM $ | Hypothetical-case as identified by sensitivity analysis  MM $ |
| Area 100: Feedstock handling | $25.7 | $27.3 | $26.8 | $27.3 |
| Area 200: Pretreatment | $9.7 | $9.9 | $22.6 | $9.9 |
| Area 300: Enzymatic Hydrolysis and Fermentation | $30.1 | $23.7 | $23.1 | $23.3 |
| Area 400: Enzyme Production | $73.7 | $30.6 | $30.5 | $25.6 |
| Area 500: Recovery | $24.3 | $23.0 | $23.1 | $22.8 |
| Area 600: Wastewater | $51.5 | $51.7 | $48.5 | $50.3 |
| Area 700: Storage | $7.0 | $6.8 | $6.8 | $6.6 |
| Area 800: Boiler/Turbogenerator | $71.3 | $65.3 | $61.3 | $64.5 |
| Area 900: Utilities | $9.8 | $8.0 | $7.1 | $7.3 |
| **Total Installed Costs** | $303.2 | $246.2 | $249.8 | $237.5 |
| Total Direct Costs (TDC) | $327.3 | $261.4 | $267.2 | $251.8 |
| Total Indirect Costs | $196.4 | $156.8 | $160.3 | $151.1 |
| **Fixed Capital Investment (FCI)** | $523.7 | $418.3 | $427.5 | $402.9 |
| Land | $1.8 | $1.8 | $1.8 | $1.8 |
| Working Capital | $26.2 | $20.9 | $21.4 | $20.1 |
| **Total Capital Investment (TCI)** | $551.7 | $441.0 | $450.8 | $424.9 |

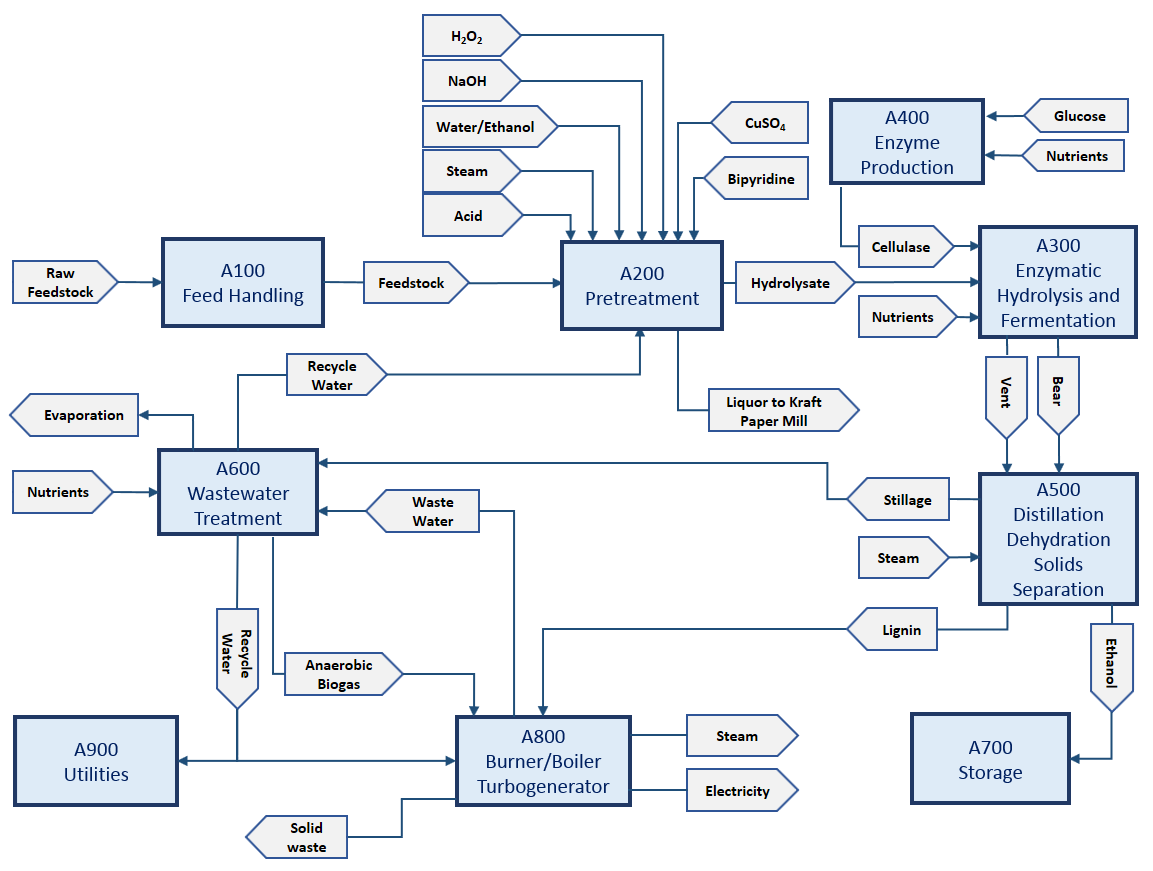
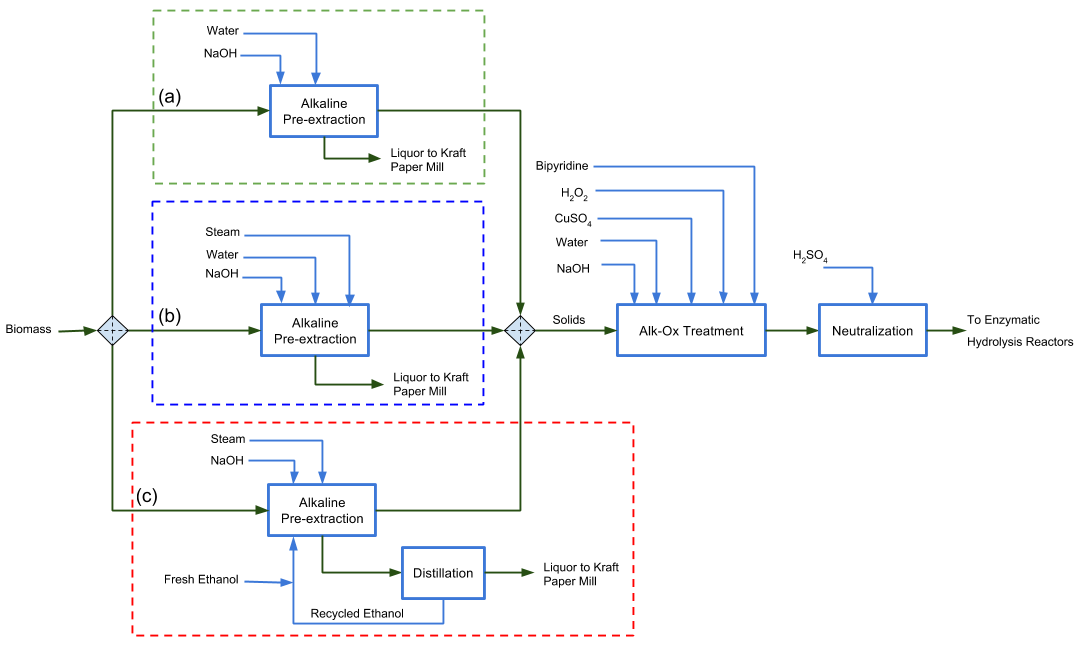


Fig. S1. Block flow diagram of the biorefinery.



**Fig. S2.** Process flow diagram of pretreatment unit including first stage (a) 30 °C NaOH-H2O PE, (b) 120 °C NaOH-H2O PE, and (c) 120 °C NaOH-EtOH PE followed by second stage Cu-AHP pretreatment.

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