Supplemental Information

This section details the calculation methods used to determine the values depicted in the Sankey diagrams for both the Py-ECH and the CE processes.
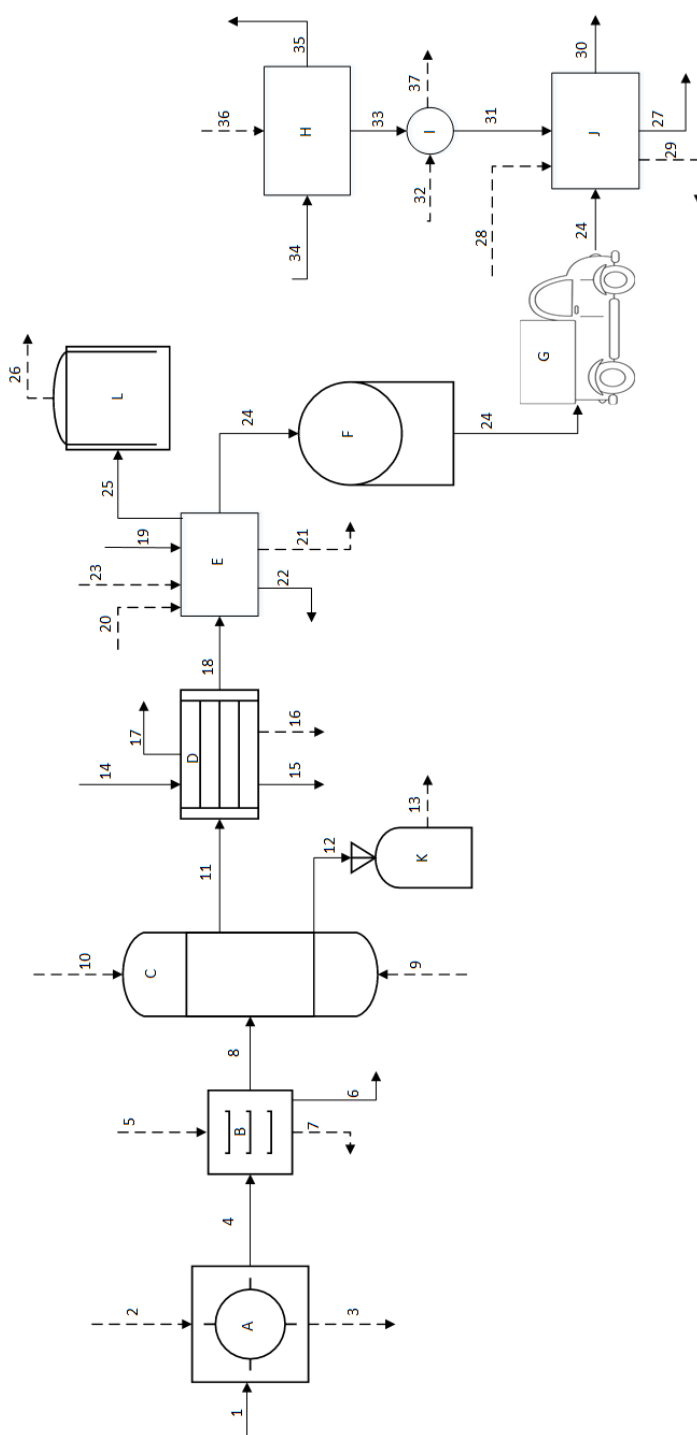
Py-ECH Process

Figure S1. Process Flow Diagram for Py-ECH Process.

Table S1. Label Definitions for the Process Flow Diagram.

Label	Process
A	Grinding
B	Drying
C	Fast Pyrolysis
D	Condensation
E	Electrocatalytic Hydrogenation
F	Fuel Storage
G	Fuel Transportation
H	Electrolysis
I	Hydrogen Compression
J	Hydroprocessing
K	Biochar Storage
L	Hydrogen Storage

1. Overview of the Process:

For the Py-ECH process, as shown in Figure S1, harvested biomass feedstock is first milled in a series of grinders (A) and then dried in a rotary dryer (B) to a moisture of 5%. The ground dry biomass (BM) is then fast pyrolyzed in a screw reactor. The biochar (BC) is collected, while the pyrolysis vapors (PyV) are condensed in a condenser (D) to produce the primary product bio-oil. The non-condensable gases (NCG) may be used for heating purposes. The bio-oil (BO) is subsequently fed into the electrocatalytic hydrogenation (ECH) unit, wherein it is chemically reduced to produce the stable bio-oil (SBO). The ECH unit (E) is considered to be a 2-compartment electrolytic cell, separated by a proton-exchange membrane. The mildly hydrogenated product from E is then transported to a petroleum refinery, where it is upgraded to a gasoline-like fuel. This upgrading occurs in a hydroprocessor unit (J) under more severe operating conditions. The compressed hydrogen gas required for the process is provided by the electrolysis of water in a local electrolyser unit (H). The product from the hydroprocessor unit is referred in the following sections as upgraded bio-oil (UBO).

2. Feedstock:

To compare the Py-ECH process to NREL's CE process, the biomass feedstock selected was corn stover. The empirical formula was determined from the ultimate analysis data for corn stover.[1] The extracted mass percentages were normalized to exclude all elements but carbon, hydrogen and oxygen. Feedstock moisture content was reduced from 20% for the raw biomass to 5% for the ground, dried biomass. The feed rate of biomass was assumed to be 1.0 billion dry tonnes/year, which is approximately the entire biomass potential of the United States, in 2030, that can be produced at $60/dry ton or less.[2] The higher heating value of corn stover was evaluated from ultimate analysis data.[1]

The feedstock data have been summarized below:

Table S2. Feedstock Data for Py-ECH.

Feedstock	Corn Stover
Empirical Formula	$CH_{1.412}O_{0.714}$
Raw biomass moisture %	20%
Dried biomass moisture %	5%
Dried biomass HHV	18.860 MJ/kg
Dried biomass feed rate	1.050 billion tonnes/year

The mass and energy balances for all primary unit operations involved in the Py-ECH process were performed as described in Section 3.

3. Major Processes
1. Calculation Methods
    A. Mass Balances: The mass values for each stream were reported in units of Billion tonnes/yr.
    B. Carbon Balances: The carbon values were reported in units of Billion tonnes C/yr.
    C. Energy Balances: The energy values were reported in units of EJ/yr. The energy balances were performed on a higher heating value basis. This implies that the energy value of each stream had three components:
        a. The higher heating value of the stream at the reference state.
        b. A sensible heat component to raise the temperature of the stream from the reference state temperature.
        c. A latent heat component for any change of phase of all or part of the stream.
    D. Reference State:
        a. The reference state was selected to be 25°C and 1 bar pressure.
    E. Higher Heating Values: The higher heating values (HHV) required for making the energy balances, were calculated using the Gaur and Reed formula:[3]

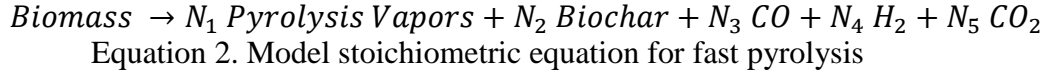$$HHV = (0.3491X_C) + (1.1783X_H) + (0.1005X_S) - (0.0151X_N) - (0.1034X_O) - (0.0211X_{ash})$$

Equation 1. Gaur and Reed Expression for calculation of HHV

Where Xi's = mass percentage and HHV is in MJ/kg.

The mass percentages were determined from ultimate analysis data provided in the literature. On certain occasions however, the HHV values were directly extracted from literature.
    a) Thermophysical Properties: The thermophysical properties like specific heat and latent heat of vaporization were extracted from the NIST database in Aspen or were estimated using Group Contribution Theory.[4-8]

b) Sample Calculation: A sample calculation is shown below for the energy balance around the pyrolysis reactor. The fast pyrolysis reaction can be modelled by the following equation:

$$Biomass \rightarrow N_1 \; Pyrolysis \; Vapors + N_2 \; Biochar + N_3 \; CO + N_4 \; H_2 + N_5 \; CO_2$$

Equation 2. Model stoichiometric equation for fast pyrolysis

Where N_i refer to the stoichiometric coefficients.

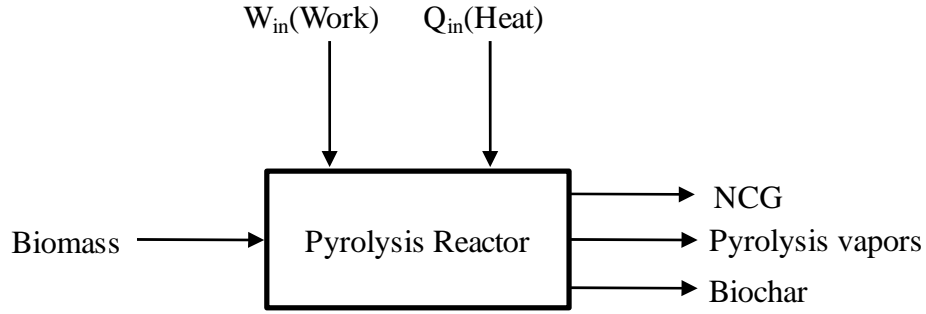Figure S2. Process Flow Diagram for Pyrolysis of Biomass.

For the reactor shown in Figure S2, the energy balance is given by:

$$m_{BM} h_{f,BM}^0 + Q_{in} + W_{in}$$
$$= m_{PyV} \left(h_{f,PyV}^0 + \left(h_{PyV} - h_{PyV,r} \right) \right) + m_{BC} \left(h_{f,BC}^0 + \left(h_{BC} - h_{BC,r} \right) \right)$$
$$+ m_{CO} \left(h_{f,CO}^0 + \left(h_{CO} - h_{CO,r} \right) \right) + m_{H_2} \left(h_{f,H_2}^0 + \left(h_{H_2} - h_{H_2,r} \right) \right)$$
$$+ m_{CO_2} \left(h_{f,CO_2}^0 + \left(h_{H_2O} - h_{CO_2,r} \right) \right)$$

$$.......................... (1)$$

Which can be rearranged to:

$$m_{BM} h_{f,BM}^0 + Q_{in} + W_{in} - \sum_i m_i \left(h_i - h_{R,i} \right)$$
$$= m_{BO} \left(h_{f,PyV}^0 \right) + m_{BC} \left(h_{f,BC}^0 \right) + m_{CO} \left(h_{f,CO}^0 \right) + m_{H_2} \left(h_{f,H_2}^0 \right)$$
$$+ m_{CO_2} \left(h_{f,CO_2}^0 \right)$$

$$..................... (2)$$

Where m_i refers to mass of the ith stream and $h_{f,i}^0$ refers to enthalpy of formation of the the ith stream.

The heat of combustion for Biomass (BM), Pyrolysis Vapors (PyV), CO, H_2 and Biochar (BC) are given by:

$$-m_{CO_2} h_{f,CO_2}^0 - m_{H_2O} h_{f,H_2O}^0 = H_{C,BM} - m_{BM} h_{BM}^0 .... (3)$$

$$-m_{CO_2} h_{f,CO_2}^0 - m_{H_2O} h_{f,H_2O}^0 = H_{C,PyV} - m_{PyV} h_{PyV}^0 .... (4)$$

$$-m_{CO_2} h_{f,CO_2}^0 - m_{H_2O} h_{f,H_2O}^0 = H_{C,BC} - m_{BC} h_{BC}^0 .... (5)$$

$$-m_{CO_2}h_{f,CO_2}^0 = H_{C,CO} - m_{CO}h_{f,CO}^0 \quad\text{...........................(6)}$$

$$-m_{H_2O}h_{f,H_2O}^0 = H_{C,H_2} - m_{H_2}h_{f,H_2}^0 \quad\text{...........................(7)}$$

Where $H_{C,i}$ refers to the heat of combustion of the ith component.

(3) to (7) are derived by considering the complete combustion of each component to CO_2 and H_2O. The heat of combustion of any compound is the negative of the enthalpy change for the combustion reaction. The standard enthalpy of formation of O_2 is zero, and therefore does not appear in (3) to (7).

Subtracting equations (4) to (7) from (3):

$$\left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{BM} - \left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{PyV}$$
$$- \left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{BC} + m_{CO_2}h_{f,CO_2}^0 + m_{H_2O}h_{f,H_2O}^0$$
$$= -H_R - m_{BM}h_{BM}^0 + m_{PyV}h_{PyV}^0 + m_{BC}h_{BC}^0 + m_{CO}h_{f,CO}^0 + m_{H_2}h_{f,H_2}^0$$
$$\text{.........(8)}$$

where $H_R = -H_{C,BM} + H_{C,PyV} + H_{C,BC} + H_{C,CO} + H_{C,H_2}$ is the heat of reaction of the pyrolysis process. The heat of combustion of carbon dioxide is zero and therefore is not included.

As $H_R = -m_{BM}h_{BM}^0 + m_{PyV}h_{PyV}^0 + m_{BC}h_{BC}^0 + m_{CO}h_{f,CO}^0 + m_{H_2}h_{f,H_2}^0 + m_{CO_2}h_{f,CO_2}^0$

also, the left hand side of (8) equals $-m_{CO_2}(h_{f,CO_2}^0)$.

Adding (8) to (2):

$$m_{BM}h_{f,BM}^0 + \left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{BM} + Q_{in} + W_{in} - \sum_i m_i(h_i - h_{R,i})$$
$$= (m_{PyV}(h_{f,PyV}^0) + \left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{PyV}) + \left(m_{BC}(h_{f,BC}^0) + \right.$$
$$\left(-m_{CO_2}h_{f,CO_2}^0 - m_{H_2O}h_{f,H_2O}^0\right)_{BC}\right) + \left(m_{CO}(h_{f,CO}^0) + m_{H_2}(h_{f,H_2}^0) - m_{CO_2}(h_{f,CO_2}^0) - \right.$$
$$\left. m_{H_2O}(h_{f,H_2O}^0)\right)$$
$$\text{.......(9)}$$

$$\Rightarrow m_{BM}HHV_{BM} + Q_{in} + W_{in} - \sum_i m_i(h_i - h_{R,i})$$
$$= m_{PyV}HHV_{PyV} + m_{BC}HHV_{BC} + m_{NCG}HHV_{NCG}$$
$$\text{...........(10)}$$

Where $m_i HHV_i = \sum_{reactants} m_i h_{f,i}^0 - \sum_{products} m_i h_{f,i}^0$ for the complete combustion reaction of the corresponding component with product water in the liquid state. Note that NCG refers to the combined stream of CO, CO_2 and H_2.

Therefore, for the pyrolysis reactor:

i. Energy associated with incoming biomass (E_{BM}):
$$m_{BM} HHV_{biomass}$$

ii. Energy associated with Pyrolysis Vapors (E_{PyV}):
$$\left(m_{PyV} HHV_{PyV} + m_{PyV}\left(h_{PyV} - h_{PyV,R}\right)\right)$$

iii. Energy associated with Biochar (E_{BC}):
$$\left(m_{BC} HHV_{BC} + m_{BC}\left(h_{BC} - H_{BC,R}\right)\right)$$

iv. Energy associated with non-condensable gases (E_{NCG}):
$$\left(m_{NCG} HHV_{NCG} + m_{NCG}\left(h_{NCG} - h_{NCG,R}\right)\right)$$

v. Work input required (W_{in}): Electrical energy required by the pyrolysis reactor.

vi. Heat required by pyrolysis (Q_{in}):
$$Q_{in} = E_{BM} - E_{PyV} - E_{BC} - E_{NCG} - W_{in}$$

Finally, both the sensible and the latent heat components are included in the $(h_i - h_{i,R})$ term.

2. Grinding

The raw biomass feedstock is ground from a size of 50 to 200 mm to about 2 mm using hammer mills. The grinding energy requirement was evaluated from literature.[9] The entire energy supplied was assumed to be lost as heat and there was no change in energy of the biomass.

Table S3. Operating Conditions for Grinding.

Temperature	25°C
Pressure	1 bar
Grinding Energy	0.215 MJ/kg of dry biomass

3. Drying

The ground biomass feedstock is dried in a rotary dryer from an initial moisture content of 20% to a final moisture content of 5%. The minimum drying energy requirement was calculated by determining the amount of heat required to evaporate moisture in the feedstock from 20% to 5%. This heat was doubled to approximate the actual energy required for the process.[10]

Table S4. Operating Conditions for the Dryer.

Temperature	100°C
Pressure	1 bar
Feed Moisture Content	20%
Product Moisture Content	5%

4. Fast Pyrolysis

In the pyrolysis screw reactor, the dried biomass is heated to a temperature of 500°C at atmospheric pressure in the absence of air. The vapor residence time is assumed to be 30

seconds. The pyrolysis products were considered to be pyrolysis vapors (forms bio-oil when condensed), biochar, and NCG, with the yields assumed as 70%, 15%, and 15% by weight respectively. The NCG was composed of only CO, CO_2 and H_2. To arrive at a stoichiometric balanced reaction for the fast pyrolysis reaction, the empirical formulae of biochar and pyrolysis vapors were determined.

a) Biochar: The empirical formula for the biochar was determined from literature.[1] The HHV was also calculated using the Gaur and Reed formula by utilizing the ultimate analysis data provided.[1]

b) Pyrolysis Vapors: In order to determine an empirical formula for the pyrolysis vapors, which is an extremely complex mixture of organic compounds, certain representative compounds were selected. The mass fractions of these representative compounds, corresponding to different functional groups were estimated from Figure S3. The mass fraction of water was assumed to be 18% and the mass fractions of the other representative compounds were normalized accordingly. The pyrolysis vapors were subsequently condensed and the condensed liquid was referred to as bio-oil. The model representative compounds and the assumed mass percentages are presented in Table S5. Subsequently, the empirical formula was determined. The HHV was once again calculated using the Gaur and Reed formula.

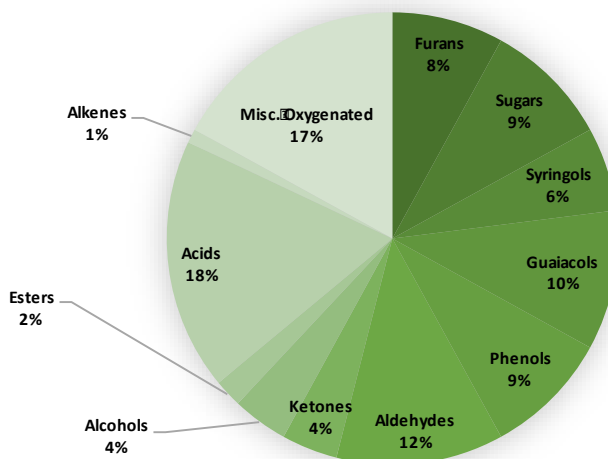c) NCG: The NCG were assumed to be composed of CO, CO_2 and H_2 only.

Figure S3. General Distribution of Functional Groups in Bio-oil.[11]

Table S5. Representative Compounds in PyV.

Compound	Mass percentage
Water	18.00
Acetic Acid	19.17

Glycolaldehyde	9.05
Phenol	9.58
Furfural	8.52
Guaiacol	10.65
Levoglucosan	9.58
Acetol	9.05

After evaluation of the empirical formulae of biochar and pyrolysis vapors, the balanced stoichiometric equation was determined as follows:
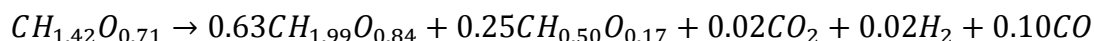
$$CH_{1.42}O_{0.71} \rightarrow 0.63CH_{1.99}O_{0.84} + 0.25CH_{0.50}O_{0.17} + 0.02CO_2 + 0.02H_2 + 0.10CO$$

Table S6. Fast Pyrolysis Data.

Temperature	500°C
Pressure	1 bar
Pyrolysis Vapor Empirical Formula	$CH_{1.99}O_{0.84}$
Biochar Empirical Formula	$CH_{0.50}O_{0.17}$
HHV of pyrolysis vapors	18.811 MJ/kg
HHV of biochar	29.594 MJ/kg

The biomass enters the reactor at 25°C and heat is provided to raise the temperature to 500°C. The products are evolved at the latter temperature. Assuming no heat loss from the reactor and calculating the electrical input required (as shown below), the heat required for pyrolysis can be calculated from the difference in enthalpy streams of the reactants and the products. While the biochar is sent to storage, the NCG and the pyrolysis gases are fed to the condenser.

The electrical energy required for rotating the auger in the pyrolysis reactor was calculated as follows:

The auger was assumed to have:[12]
- Shaft Diameter (d_s) = 0.064m
- Flight Diameter (d_f) = 0.25m
- Pitch length (l_p) = 0.229m

As the density of corn stover (ρ) is 90 kg/m^3,[13] a 100 dry ton/day facility corresponds to a volumetric flow rate of about 0.7 m^3/min. Using the relation,

$$Q_a = A * l_p * n * \eta$$

where Q_a is the actual volumetric flow rate in m^3/min; A is the cross-sectional area occupied by the reacting material in m^2; n is the rotations per minute, and η is the volumetric efficiency (the ratio of actual and theoretical volumetric flow rates).[14]

Therefore,

$$Q_a = \left(\frac{\Pi}{4}\right) * \left(d_f^2 - d_s^2\right) * l_p * n * \eta$$

Assuming a volumetric efficiency of 35%, n can be evaluated to be approximately 200 rpm, which corresponds to about 3 kW of power.[13] This scales up to about 0.003 EJ/yr for processing 1 Billion tonnes/year of dry corn stover.

It must also be noted that the reactor length required for a residence time of 30s and a pitch of 0.229m for the 100 ton/day reactor was found to be less than 75 ft, which is a feasible reactor length.[15]

Figure S4 shows the streams entering and leaving the pyrolysis reactor, information on the energy content, mass content, and carbon content is given in the tables at the end of the Supplemental Information (SI).
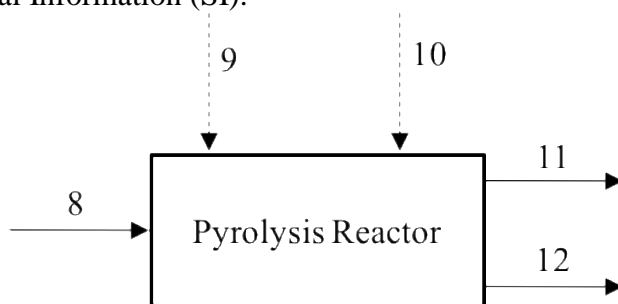
Figure S4. Process Flow Diagram for Pyrolysis.

5. Condensation
Well water entering at 13.33°C and leaving at 20°C was assumed in order to cool the entering gases from 500°C to 25°C.[16] The condensed pyrolysis vapors formed the bio-oil, whereas the NCG gases were separated. The NCG gases contain energy and may be burned to heat the pyrolysis reactor. Heat losses are considered in the condenser.

Table S7. Condensation Data.

Empirical formula of condensed Bio-oil	$CH_{1.99}O_{0.84}$
HHV of formed bio-oil	18.811 MJ/kg
Inlet temperature of cooling water	13.33°C
Outlet Temperature of Cooling water	20°C

The streams entering and leaving the condenser are shown in Figure S5.
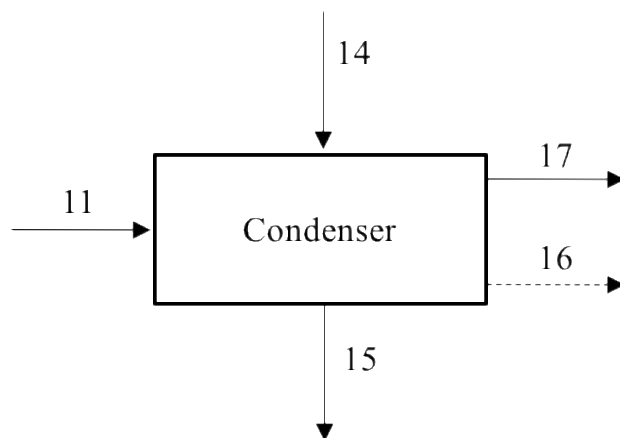
Figure S5. Condenser Flow Diagram.

6. Electrocatalytic Hydrogenation

The condensed bio-oil was fed to the ECH unit, where it was electrocatalytically hydrogenated to stable bio-oil (SBO). As this is only a thermodynamic model, the ECH unit was assumed to be a 2-compartment electrolytic cell, separated by a Nafion-117 membrane. Oxidation was performed at the Pt anode and reduction at the Ru cathode, which is supported on Activated Carbon Cloth (ACC).[17] The apparatus considered is shown in Figure S6.

Anode: $\left(\frac{n}{2}\right) H_2O \rightarrow \left(\frac{n}{4}\right) O_2 + nH^+ + ne^-$

H^+

Proton Exchange Membrane

Cathode:
$\left(\frac{n}{3}\right) H^+ + \left(\frac{n}{3}\right) e^- \rightarrow \left(\frac{n}{6}\right) H_2$

$BO + \left(\frac{2n}{3}\right) H^+ + \left(\frac{2n}{3}\right) e^- \rightarrow SBO$
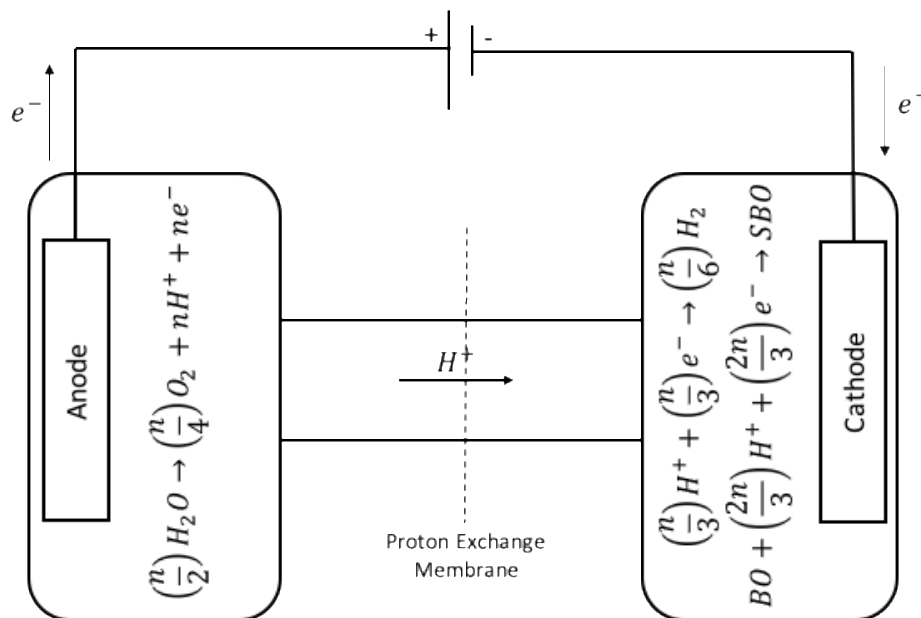
Figure S6. Schematic of ECH Apparatus.

The ECH unit uses external electrical power to split water into oxygen and H^+ ions at the anode. These H^+ ions then migrate through the Nafion membrane (a proton exchange membrane) and hydrogenate the bio-oil at the catalytic cathode. An undesirable side reaction involving the evolution of H_2 was also considered at the cathode. In summary, the reactions involved at the cathode and anode are as follows:

10

Cathode Reactions:

$$\text{1)} \quad \text{Bio-oil} + \frac{2n}{3}\,\text{H}^+ + \frac{2n}{3}\,\text{e}^- \rightarrow \text{Stable bio-oil}$$

$$\text{2)} \quad \frac{n}{3}\text{H}^+ + \frac{n}{3}\text{e}^- \rightarrow \frac{n}{6}\text{H}_2$$

Anode Reaction:

$$\frac{n}{2}\text{H}_2\text{O} \rightarrow n\text{H}^+ + n\text{e}^- + \frac{n}{4}\text{O}_2$$
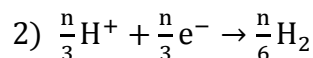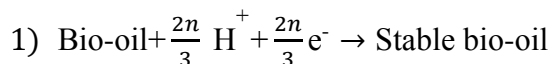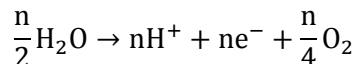
Where n is the number of moles of hydrogen ions required to reduce 1 mole of bio-oil to stable bio-oil.

To find the value of n, the empirical formula of SBO was determined. Here too, certain representative compounds were selected. These compounds were selected such that they result from the hydrogen addition to one or more compounds selected as part of the bio-oil mixture. The mass fractions for SBO were evaluated from the stoichiometry of these hydrogen addition reactions by knowing the mass fractions of the representative compounds in the bio-oil. During this reaction, only the number of H atoms changed in the empirical formula of bio-oil to make SBO, as only hydrogen addition takes place. The value of n was then determined by balancing the cathode reaction (1).

Assuming a current efficiency (electrons in desired products divided by total electrons passed) equal to 67%, the needed water splitting and the amount of H_2 liberated were calculated. Using Group Contribution Theory to estimate the Gibbs free energies for the reduction reaction for each species, the minimum external voltage required for the ECH of bio-oil was found to be 1.07V. To account for the resistance associated with the electrolyte, the electrode overpotentials, and the required activation energies, this voltage value was increased to a value of 1.43V, by assuming a voltage efficiency of 75%. The power consumption was then determined by the following formula:[18]

$$P_W = (i * V)$$

Where i is current, V is applied voltage, and P_W is the power consumption.

The assumed operating conditions and the empirical formulae determined for the BO and the SBO are presented in Table S8.

Table S8. Key Data for ECH.

Temperature	80°C
Pressure	1 bar
Bio-oil Empirical Formula	$CH_{1.99}O_{0.84}$
Stable Bio-oil Empirical Formula	$CH_{3.01}O_{0.84}$
Stable Bio-oil Model Compounds	Water, methanol, ethanol, levoglucosan, propylene glycol, ethylene glycol, furfuryl alcohol and cyclohexanol

The reactions considered for the hydrogenation of bio-oil to stable bio-oil are presented in Figure S7.
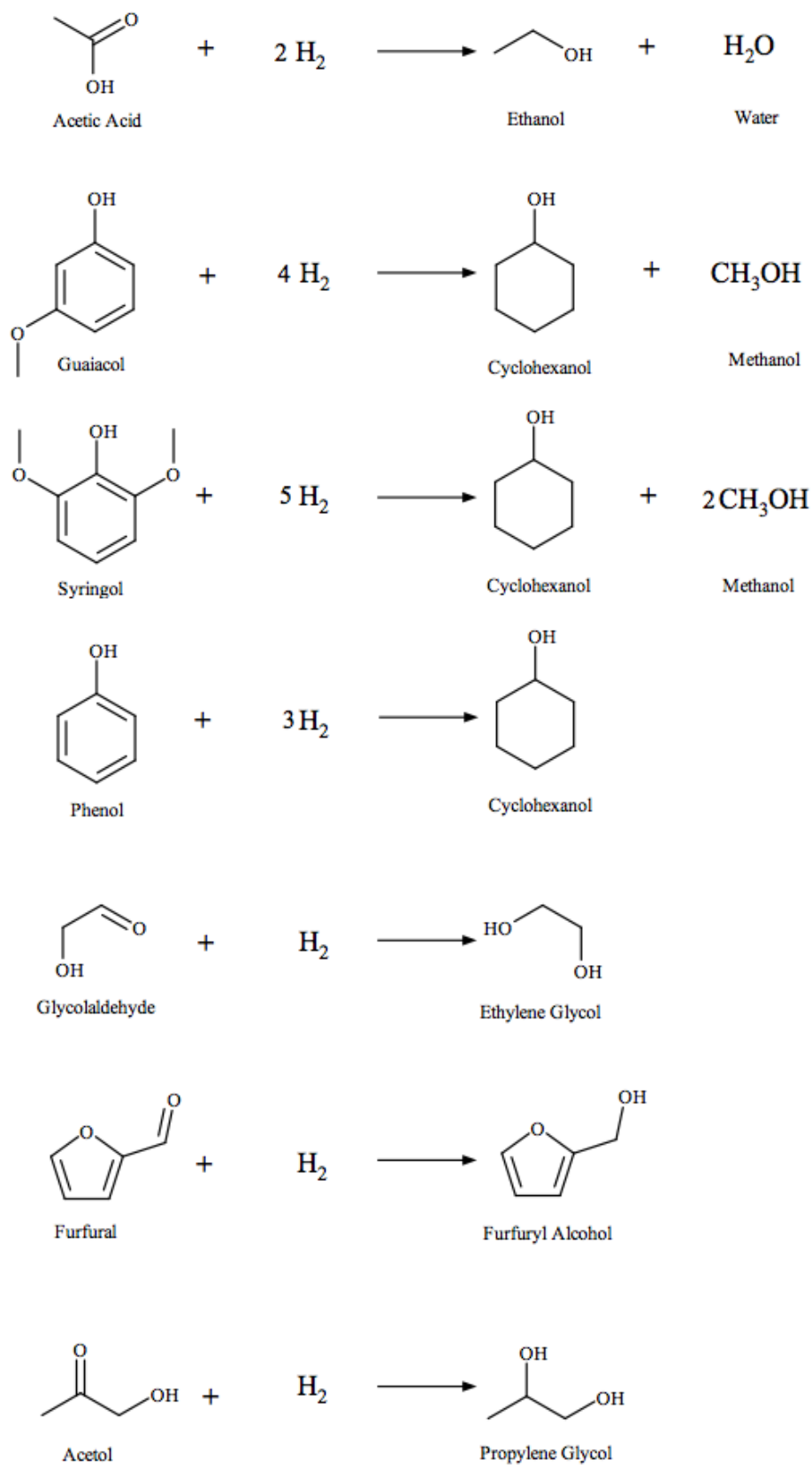
Figure S7. ECH Reactions Considered in this Analysis.

The balanced overall chemical reaction for the ECH reaction is given as:
$$CH_{1.99}O_{0.84} + 0.51H_2 \rightarrow CH_{3.01}O_{0.84}$$
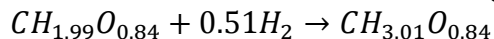
A heat input was considered for the ECH reactor to raise the temperature of the reactant streams to the required temperature. Heat losses were considered in the ECH reactor. A schematic showing the input and output streams to the ECH reactor is shown in Figure S8.
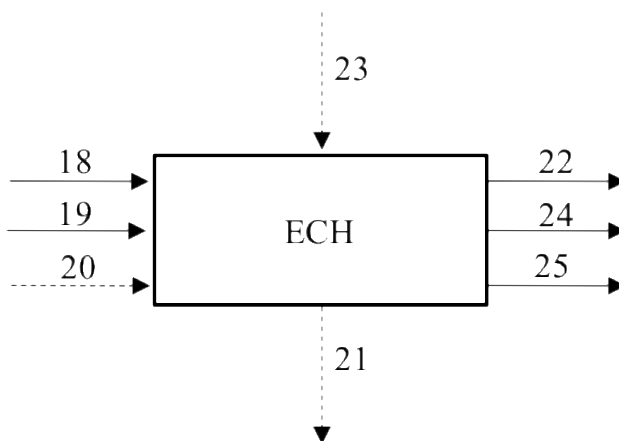
Figure S8. Process Flow Diagram for ECH.

7. Hydroprocessing

SBO is transported from the depot to a centralized refinery for hydroprocessing. In the hydroprocessor, the SBO is reacted with H_2 at elevated temperatures and pressures. For simplicity, hydroprocessing was assumed to only produce octane and water at these extreme conditions.

The overall balanced reaction for hydroprocessing was determined as:
$$CH_{3.01}O_{0.84} + 0.46H_2 \rightarrow 0.13C_8H_{18} + 0.84H_2O$$
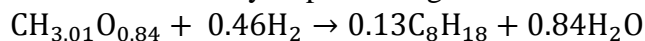
Heat was provided to the reactants to achieve the desired temperature. The hydrogen gas required for the process was supplied by performing the electrolysis of water.

The operating conditions for the hydroprocessor are provided in the Table S9.

Table S9. Hydroprocessing Data.

Temperature	400°C
Pressure	20 bar
Empirical Formula of SBO	$CH_{3.01}O_{0.84}$
Empirical Formula of UBO	C_8H_{18}

A schematic for the hydroprocessing unit is shown in Figure S9.
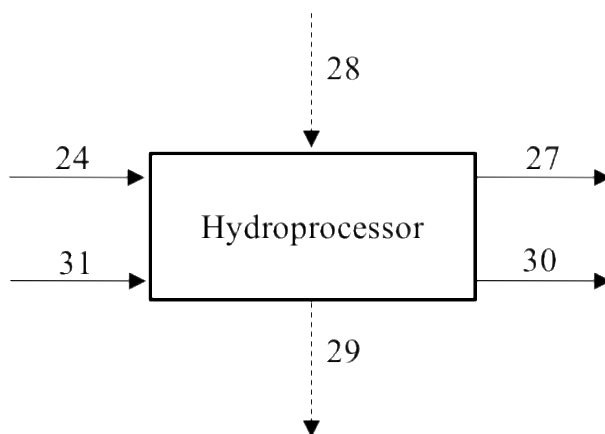
Figure S9. Hydroprocessor Process Flow Diagram.

8. Electrolysis

Electrolysis was used to provide the hydrogen needed by hydroprocessing at the petroleum refinery. The minimum external voltage required was assumed to be 1.23 V, corresponding to electrolysis of water. Here too, the voltage efficiency was assumed to be 75%.[19] The current efficiency is not applicable here since hydrogen evolution is the only reaction occurring at the cathode. The electrical energy required for the process and the required heat input to raise the reactant temperatures to the reactor temperature were calculated in the same way as for ECH. The operating conditions for the electrolysis unit are given in the Table S10.

Table S10. Electrolysis Operating Conditions.

Temperature	80°C
Pressure	1 bar

The electrolysis unit is followed by a compressor, which isothermally compresses the produced H_2 to a pressure of 200 bar, which is then fed to the hydroprocessing reactor.

9. Storage

Storage heat losses have been considered for the biochar storage and hydrogen gas storage. These have been determined by estimating the amount of heat liberated when the stored substance thermally equilibrates with the surroundings. The surrounding temperature was assumed to be 25°C at atmospheric pressure.

10. Heat Integration

No external heat source is required for the Biomass Upgrading Depot (BUD), as the evolved NCG and H_2 gases have sufficient combustion energy to provide heat to the BUD. Biochar that is not needed for combustion energy can be land applied to sequester carbon. Finally, the air requirement and the composition of the stack gas for the required combustor at the BUD is detailed in Table S12.

The heat needed to preheat the stable bio-oil feed may, in part, be provided by recycling thermal energy present in the water vapor product that exits the hydroprocessor. Heat can also be transferred from the hydroprocessor itself during its operation.

The most important values to construct the Sankey diagrams for the Py-ECH process are listed in Table S11. The stream numbers mentioned in Table S11, correspond to the stream numbers used through Figures S4, S5, S8 and S9.

CE Process

For the CE (cellulosic ethanol) process, all values were extracted from the 2011 NREL report detailing the cellulosic ethanol biorefinery.[20] The extracted values are listed in Table S13. These values were then normalized to the scale assumed for the Py-ECH process, to enable a fair comparison. The Sankey diagrams for the CE process were drawn for the entire system upon formulating overall mass, energy and carbon balances, as shown in Tables S14-16. The water balance for the CE process is included in Table S17.

Stream Tables

This section lists the carbon, energy and mass values of all streams involved in the different bioenergy systems, i.e. Py-ECH and CE. Tables S11 and S12 are for the Py-ECH process, whereas Tables S13-17 cover the CE process.

Table S11. Stream Table for Py-ECH Process.

Stream	Content	Mass	Carbon	Energy	Temperature	Pressure
		Billion tonnes	Billion tonnes C	EJ	°C	bar
1	Grinder Biomass In	1.250	0.509	20.623	25.000	1.000
2	Grinding Work In			0.215		
3	Grinding Heat Loss			0.215		
4	Dryer Biomass In	1.250	0.509	20.623	25.000	1.000
5	Drying Heat In			0.898		
6	Dryer Water Vapor Out	0.197		0.448	100.000	1.000
7	Drying Heat Loss			1.219		
8	Dryer Biomass Out	1.053	0.509	19.854	100.000	1.000
9	Pyrolysis Heat In			1.553		
10	Pyrolysis Work In			0.003		
11	Pyrolysis (Py Vapors + NCG) Out	0.895	0.384	16.671	500.000	1.000
12	Pyrolysis Biochar Out	0.158	0.125	4.738	500.000	1.000

13	Storage Pyrolysis Biochar Heat Loss			0.065		
14	Condenser Cooling Water In	0.149		-0.134	13.333	1.000
15	Condenser Cooling Water Out	0.149		-0.056	20.000	1.000
16	Condenser Heat Loss			1.324		
17	Condenser NCG Out	0.158	0.061	1.408	25.000	1.000
18	ECH Bio-Oil In	0.737	0.323	13.861	25.000	1.000
19	ECH Water In	0.369		0.000	25.000	1.000
20	ECH Work In			5.639		
21	ECH Heat Loss			0.590		
22	ECH Oxygen Out	0.328		0.017	80.000	1.000
23	ECH Heat In			0.125		
24	ECH Stable Bio-oil Out	0.764	0.323	17.087	25.000	1.000
25	ECH Hydrogen Out	0.014		1.931	80.000	1.000
26	Storage ECH Hydrogen Heat Loss			0.011		
27	Hydroprocessor Water Out	0.405		1.284	25.000	1.000
28	Hydroprocessor Heat In			1.524		
29	Hydroprocessor Heat Loss			2.418		
30	Hydroprocessor Fuel Out	0.383	0.323	18.403	25.000	1.000
31	Hydroprocessor H2 In	0.025		3.494	25.000	200.000
32	Compressor Work In			0.161		
33	Electrolysis Hydrogen Out	0.025		3.494	25.000	1.000
34	Electrolysis Water In	0.221		0.000	25.000	1.000
35	Electrolysis Oxygen Out	0.197		0.000	25.000	1.000
36	Electrolysis Work In			3.892		
37	Compressor Heat Loss			0.161		

Table S12. Balance on Combustor for Heat Integration in BUD for Py-ECH Process.

COMPONENT	SOURCE	Description	Qty.	Total
			IN	
COMPONENT	SOURCE	Description	Qty.	Total
			Billion tonnes/yr	Billion tonnes/yr
Air	External	Nitrogen	0.661	
		Oxygen	0.199	
		Water Vapor	0.017	
			0.877	0.877
NCG	Pyrolysis	CO	0.118	
		CO2	0.039	
		H2	0.001	
			0.158	0.158
H2	ECH		0.007	0.007
				1.041
			OUT	
COMPONENT	SOURCE	Description	Qty.	Total
			Billion tonnes/yr	Billion tonnes/yr
Stack Gas	Combustor	N2	0.661	
		O2	0.066	
		CO2	0.224	
		H20	0.091	
			1.041	1.041
BALANCE				0.000

Table S13. Extracted Stream Table for CE Process (Stream Numbers Correspond to NREL Report, 2011).

I/O	Component	Stream		Mass (calc)	Carbon	Energy	Temp.	Pressure
				kg/hr	kmol C/hr	Gcal/hr	°C	atm
Input	Hydrolysis & Fermentation Chemicals	309.00	CSL	211.00			20.00	1.00
		311.00	CSL	948.00			20.00	1.00
		310.00	DAP	26.00			20.00	1.00
		312.00	DAP	116.00			20.00	1.00
			Total	1,301.00	22.00	-2.00		
Input	Pre-Treatment Chemicals	273.00	NH3	1,051.00			20.00	9.00
		710.00	CSL	1,981.00			21.00	5.40
			Total	3,032.00	0.00	-3.00		

Input	Biomass Feedstock	105.00		104,167.00	3,117.00	-316.00	25.00	1.00
Input	Air for Recovery	-		12,105.00			-	-
Input	Glucose for Enzyme Production	401.00		2,845.00	81.00	-8.00	28.00	1.00
Input	Enzyme Production Chemicals	404.00	CSL	8.00			20.00	1.00
		443.00	CSL	157.00			20.00	1.00
		406.00	NH3	6.00			28.00	9.00
		441.00	NH3	109.00			28.00	9.00
		440.00	Nutrients	67.00			20.00	1.00
		442.00	SO2	16.00			28.00	3.00
		446.00	Antifoam	13.00			20.00	3.20
			Total	376.00	6.00	-1.00		

Input	Air for Enzyme Production	-		32,853.00				
Input	Air for WWT	-		223,602.00				
Input	WWT Chemicals	632.00	Caustic	4,504.00	0.00	2.00	20.00	2.00
Input	Air for Boiler/ Turbogenerat or	-		284,495.00				
Input	Chemicals for Boiler/Turbo generator	851.00	Lime	895.00	0.00	0.00	25.00	1.00
Input	Well water	904.00		147,140.00	0.00	87.00	33.00	5.00
Output	Recovery Vent	550.00		21,398.00	471.00	0.00	34.00	0.90
Output	Ethanol	515.00		21,808.00	941.00	-139.00	35.00	2.50
Output	Recovery Heat Loss					-24.00		
Output	Enzyme Production Vent	435.00		1,586.00			25.00	1.00

		423.00		31,801.00			28.00	1.00
			Total	33,387.00	54.00	0.00		
Output	WWT Evaporation	622.00		221,417.00	88.00	-1.00	25.00	1.00
Output	Brine	627.00		9,929.00	4.00	8.00	100.00	1.00
Output	WWT Heat Loss					-26.00		
Output	Boiler/Turbo generator Heat Loss					-12.00		
Output	Electricity Out					-11.00		
Output	Electricity Rsrv					-4.00		
Output	Stack & Ash	809.00	Ash	5,725.00			0.00	1.00
		810.00	Stack	363,445.00			145.00	1.00
		821V	Stack-2	2,580.00			100.00	1.00

			Total	371,750.00	1,680.00	-12.00		
Output	Cooling Tower	-		137,362.00	0.00	-20.00	37.00	1.00

Table S14. Energy Balance for CE Process as Plotted on Sankey Diagram.

IN					
COMPONENT	**SOURCE**	**Description**	**Qty.**	**Norm.**	**Total**
			(Gcal/hr)	(EJ/yr)	(EJ/yr)
Biomass		Raw Feedstock	-316.000	20.623	20.623
Chemicals	Fermentation	CSL, DAP	-2.000	0.131	
	Pre-treatment	Ammonia, dil. Sulfuric Acid	-3.000	0.196	
	Enzyme Production	CSL, Ammonia, SO2, Corn Oil	-1.000	0.065	
	WWT	Caustic	2.000	-0.131	
	Boiler/ Generator	Lime in FGD, Ammonia, Phosphate	0.000	0.000	0.261
Glucose		Glucose for Enzyme Production	-8.000	0.522	0.522
Air	Recovery		0.000	0.000	
	Enzyme		0.000	0.000	
	WWT		0.000	0.000	
	Boiler/Generator		0.000	0.000	0.000
					21.406
OUT					
COMPONENT	**SOURCE**		**Qty.**	**Norm.**	**Total**
			(Gcal/hr)	(EJ/yr)	(EJ/yr)
Ethanol			-139.000	9.071	9.071
Electricity	Out		-11.000	0.718	
	Reserve		-4.000	0.261	0.979
Losses	Recovery Heat Loss	Heat Loss	-24.000	1.566	

	WWT Heat Loss	Heat Loss	-26.000	1.697	
	Boiler/Generator Heat Loss	Heat Loss	-12.000	0.783	
	CW Heat Loss	Heat Loss	-107.000	6.983	11.029
Vents &Waste Streams	Recovery Vent		0.000	0.000	
	Enzyme Production Vent		0.000	0.000	
	Boiler Stack & Ash	CO2,CO,SOX, NOX, H2S,O2, N2,NH3	-12.000	0.783	
	WWT Evaporation	CO2,CO,SOX, NOX, H2S,O2, N2, CH4	-1.000	0.065	
	WWT Brine	Predominantly NaNO3	8.000	-0.522	0.326
					21.406
BALANCE					**0.000**

Table S15. Mass Balance for CE Process as Plotted on the Sankey Diagram.

IN						
COMPONENT		**SOURCE**	**Stream No.**	**Qty.**	**Norm.**	**Total**
				(kg/hr)	Billion tonnes/yr	Billion tonnes/yr
Oxygen		Air for Enzyme Production	450	7440.00	0.09	
		Air for Recovery Section	559	2764.00	0.03	
		Air for WWT	630	51061.00	0.61	
		Air for Boiler	804	64966.00	0.78	
					1.51	1.51
Nitrogen		Air for Enzyme Production	450	24504.00	0.29	
		Air for Recovery Section	559	9104.00	0.11	

		Air for WWT	630	168162.00	2.02	
		Air for Boiler	804	213957.00	2.57	
					4.99	4.99
Water		Air for Enzyme Production	450	638.00	0.01	
		Air for Recovery Section	559	237.00	0.00	
		Air for WWT	630	4379.00	0.05	
		Air for Boiler	804	5572.00	0.07	
		Feedstock	105	20833.00	0.25	
		Fermentation Chemicals	309,310,311, 312	582.00	0.01	
		Pre-Treatment Chemicals	273,710	139.00	0.00	
		Glucose Solution	401	427.00	0.01	
		Enzyme Production Chemicals	404,443,406, 441,440	83.00	0.00	
		Wastewater Chemicals	632	2252.00	0.03	
		Well Water	904	147140.00	1.77	
					2.19	2.19
Glucose		Glucose Soln.	401	2418.00	0.03	0.03
Chemicals	Protein	Fermentation Chemicals	309,310,311, 312	290.00	0.00	
		Enzyme Chemicals	404,443,406, 441,440	41.00	0.00	
	Ammonia	Pre-Treatment Chemicals	273,710	1051.00	0.01	
		Enzyme Chemicals	404,443,406, 441,440	115.00	0.00	

COMPONENT		SOURCE	Stream No.	Qty.	Norm.	Total
	Sulfuric Acid	Pre-Treatment Chemicals	273, 710	1842.00	0.02	
					0.04	0.04
Dry Biomass		Feedstock	105	83334.00	1.00	1.00
Other Solids		Fermentation Chemicals	309,310,311, 312	429.00	0.01	
		Enzyme Production Chemicals	404,443,406, 441,440	108.00	0.00	
		Wastewater Chemicals	632	2252.00	0.03	
		Boiler Chemicals	851	895.00	0.01	
					0.04	0.04
						9.80

			OUT			
COMPONENT		**SOURCE**	**Stream No.**	**Qty.**	**Norm.**	**Total**
				(kg/hr)	Billion tonnes/yr	Billion tonnes/yr
Oxygen		WWT Evaporation	622	44765.00	0.54	
		Stack & Ash	809,810,821 V	11324.00	0.14	
		Enzyme Production Vent	435,423	5727.00	0.07	
		Recovery Vent	550	172.00	0.00	
					0.74	0.74
Nitrogen		WWT Evaporation	622	168157.00	2.02	
		Stack & Ash	809,810,821 V	223985.00	2.69	
		Enzyme Production Vent	435,423	24504.00	0.29	

					5.00	5.00
Water		WWT Evaporation	622	4350.00	0.05	
		Stack & Ash V	809,810,821	57031.00	0.68	
		Brine	627	4967.00	0.06	
		Enzyme Production Vent	435,423	774.00	0.01	
		Recovery Vent	550	522.00	0.01	
		Cooling Tower Evaporation	948 - 949	138293	1.66	
		Product	519	108.00	0.00	
					2.47	2.47
Chemicals	CO/NOx/SOx/H2S	WWT Evaporation	622	284.00	0.00	
		Stack & Ash V	809,810,821	178.00	0.00	
		Brine	627	44.00	0.00	
	Ammonia	WWT Evaporation	622	1.00	0.00	
		Stack & Ash V	809,810,821	30.00	0.00	
		Brine	627	3.00	0.00	
	Methane	WWT Evaporation	622	3.00	0.00	
					0.01	0.01
CO2		WWT Evaporation	622	3857.00	0.05	
		Stack & Ash V	809,810,821	73396.00	0.88	
		Enzyme Production Vent	435,423	2382.00	0.03	
		Recovery Vent	550	20669.00	0.25	
					1.20	1.20

Ethanol		Product	519	21673.00	0.26	0.26
Other Solids		Stack & Ash	809,810,821 V	5805.00	0.07	
		Brine	627	4907.00	0.06	
					0.13	0.13
						9.81
BALANCE						**-0.01**

Table S16. Carbon Balance for CE Process as Plotted on the Sankey Diagram.

IN				
COMPONENT	**SOURCE**	**Qty.**	**Norm.**	**Total**
		(kmol/hr)	Biilion tonnes/yr	Billion tonnes/yr
Biomass		3117.000	0.509	0.509
Chemicals	Fermentation	22.000	0.004	
	Pre-treatment	0.000	0.000	
	Enzyme Production	6.000	0.001	
	WWT	0.000	0.000	
	Boiler/ Generator	0.000	0.000	0.005
Glucose		81.000	0.013	0.013
				0.526
OUT				
COMPONENT	**SOURCE**	**Qty.**	**Norm.**	**Total**
		(kmol/hr)	Biilion tonnes/yr	Billion tonnes/yr
Ethanol		941.000	0.154	0.154
CO2 and traces	Recovery Vent	471.000	0.077	
	Enzyme Production Vent	54.000	0.009	
	WWT Evaporation	88.000	0.014	
	Brine	4.000	0.001	
	Stack & Ash	1680.000	0.274	0.375

				0.528
BALANCE				**-0.002**

Table S16. Water Balance for CE Process as Plotted on the Sankey Diagram.

	Water Balance				
	Component	**Stream No.**	**Qty.**	**Norm.**	**Total**
In	Air for Enzyme Production	450	638.00	0.01	
	Air for Recovery Section	559	237.00	0.00	
	Air for WWT	630	4379.00	0.05	
	Air for Boiler	804	5572.00	0.07	
	Feedstock	105	20833.00	0.25	
	Fermentation Chemicals	309,310,311,312	582.00	0.01	
	Pre-Treatment Chemicals	273,710	139.00	0.00	
	Glucose Solution	401	427.00	0.01	
	Enzyme Production Chemicals	404,443,406,441,440	83.00	0.00	
	Wastewater Chemicals	632	2252.00	0.03	
	Well Water	904	147140.00	1.77	
				2.19	**2.19**
Out	WWT Evaporation	622	4350.00	0.05	
	Stack & Ash	809,810,821V	57031.00	0.68	
	Brine	627	4967.00	0.06	
	Enzyme Production Vent	435,423	774.00	0.01	
	Recovery Vent	550	522.00	0.01	
	Cooling Water Evaporation	948 - 949	138293.00	1.66	
	Product	519	108.00	0.00	
				2.47	**2.47**
Generated	Enzyme Production		1291	0.02	
	Fermentation	Table 37	121	0.00	
	WWT		2680	0.03	
	Combustor		23869	0.29	
				0.34	**0.34**
Consumed	Pretreatment	Table 37	2473	0.03	
	Enzymatic Hydrolysis		2631	0.03	
				0.06	**0.06**

Balance				**-0.01**

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