Supplementary material

Integrated process simulation for bioethanol production: Effects of varying lignocellulosic feedstocks on technical performance

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1. Determination of forest residues composition

The biomass of each component of the tree were estimated from BEF (Biomass Expansion Factors, in Mg·m⁻³ stem under bark) using Equation S.1 (Lehtonen et al., 2004), where \( a_i \) and \( b_i \) are parameters, \( t \) is the stand age (in years) and \( i \) is the biomass component: stem, foliage, living branches, dead branches, stump, coarse roots, small roots). Values are defined in Table S.1. One rotation period is assumed of 100 and 60 years, for Norway Spruce and Birch sp., respectively.

\[
BEF_i = a_i + b_i e^{-0.01t}
\]

Eq. S.1

**Table S.1.** BEF for Norway Spruce and Birch sp. (Lehtonen et al., 2004)

| Tree component                          | Norway Spruce (a) | Norway Spruce (b) | Birch sp. (a) | Birch sp. (b) | BEF     |
|-----------------------------------------|-------------------|-------------------|---------------|---------------|---------|
| Stem                                    | 0.4               | -0.0462           | 0.3830        | 0.3964        | -0.0186 | 0.3862  |
| Foliage                                 | 0.0388            | 0.0849            | 0.0700        | 0.025*        | 0.0119  |
| Branches, alive                         | 0.0085            | 0.0719            | 0.1170        | 0.1011        | -0.018  | 0.0912  |
| Branches, dead                          | 0.0088            | 0.004             | 0.0103        | 0.0053        | 0.0082  | 0.0098  |
| Stump                                    | 0.0488            | 0.0044            | 0.0504        | 0.0472        | -0.0039 | 0.0451  |
| Roots, coarse > 5 cm                    | 0.1024            | -0.0271           | 0.0924        | 0.042*        | 0.0420  |
| Roots, small < 5 cm                     | 0.0201            | 0.0448            | 0.0366        | 0.042*        | 0.0420  |

Note: * update based on (Hömaili et al., 2003) for foliage and (de Wit et al., 2006) for roots estimation.

The annual mass produced \( (m_{\text{annual}i}, \) ton·y⁻¹) for each biomass component \( i \), is calculated by the equation S.2, where \( f_i \) is the extraction factor (percentage collected of component \( i \)) and \( V_{\text{annual, specie}} \) is the volume produced annually of each forestall specie. \( V_{\text{annual, specie}} \) considers 1 m³·y⁻¹ as base, for Norway Spruce and Birch.

\[
m_{\text{annual}i} = \text{BEF}_i \cdot f_i \cdot V_{\text{annual, specie}}
\]

Eq. S.2

The forest residues are mainly composed by stem bark, branches, foliage, needles, stumps and roots. However, in this study only above-ground components, i.e. foliage and branches, are considered as available residues to be used as feedstock for ethanol production, excluding the bark and under-ground residues (stumps and roots). Other assumption is related to the extraction factor \( (f_i) \) for these compounds, considering 75% of total foliage is collected for Spruce and Birch, while 75% and 50% of the branches (alive and dead) are collected for Spruce and Birch, respectively. These assumptions can be traduced as a collection of 30% and 35% of the total potential residues for Spruce and Birch, respectively. This study used foliage and branches as forest residues (detailed in Table S.2).

**Table S.2.** Percent by residue components.

| Tree component | Norway Spruce | Birch sp. |
|----------------|---------------|-----------|
| Foliage        | 45.23 %       | 10.57 %   |
| Branches, alive| 54.77 %       | 89.43 %   |

Table S.3 summarizes the variation in the composition, such as lignin, glucan, xylan, among others, by each tree component (see Figure S.1 for a more graphical representation).

**Table S.3.** Proportions of the main chemical compounds (%) within tree biomass components

| % DM basis | Stem | Foliage | Branches | Bark | Stump | Roots |
|------------|------|---------|----------|------|-------|-------|
| Cellulose  | 41.4 | 38.5    | 38.5     | 31.4 | 42.8  | 42.8  |
| Xylan      | 5.4  | 5.1     | 5.1      | 4.2  | 5.6   | 5.6   |
| Arabinan   | 1.2  | 1.8     | 1.8      | 3.3  | 0.9   | 0.9   |
| Galactan   | 1.4  | 1.4     | 1.4      | 1.2  | 1.5   | 1.5   |
| Mannan     | 9.4  | 8       | 8        | 4.5  | 10.1  | 10.1  |
| Lignin     | 34.2 | 34.1    | 34.1     | 33.9 | 34.3  | 34.3  |
| Ash        | 0.6  | 1.1     | 1.1      | 2.3  | 0.3   | 0.3   |
| Acetate    | 1.1  | 0.8     | 0.8      | 0.3  | 1.2   | 1.2   |
| Extractives| 5.3  | 9.2     | 9.2      | 18.9 | 3.3   | 3.3   |
| Ash, non-ident.| -    | -       | -        | -    | -     | -     |

Table of ^{Nurmi, 1997; Räisänen & Athanassiadis, 2013}.
Finally, the general composition of the biomass residues of Norway Spruce and Birch summarizes in Table S.1 (in article) are obtained multiplying the percent of each residual element (branches and foliage) in Table S.2 by the percent of every chemical compound (for foliage and branches) defined in Table S.3.
2. Storage and chopping

A simplified process flow diagram is shown in Figure S.2. The storage and chipping area operate at the same capacity of the biorefinery, i.e., 128,000 kg biomass·h\(^{-1}\). To satisfy production requirements, the plant must receive 10 dumper trucks (13 t capacity, compliant with EURO6 emissions standards), every hour. The trucks are unloaded using the dumper, requiring ~10 min for unloading. The dumpers empty into hoppers, which send the biomass to a series of conveyors to a coverage storage section. Two storage domes (each with a 36-hour capacity) are required, so that one can be loaded while the other is empty to the conversion process. The distribution of biomass inside the storage domes is carried out by wheel loaders (2 units by storage dome), which also load the conveyors belts to transport the biomass to the chippers. Two different chippers are used in this section, chipper 1 reduces the size to 400 mm chip-length and chipper 2 mills to 40 mm chip-length size. A disc scalping screen is used to screening large and oversize biomass chips, to be returned to the chipper 2. Finally, the biomass is stored in a chip silo with a discharger to control the biomass flow delivered to the pretreatment process.

Figure S.2. Detailed description of the storage and chipping.

Table S.4 List of the technical specifications for the machinery used in the process. Two units are required for most of the machinery, so we can assume two production lines working at the same time. Table S.5 summarizes the inventory to produce 1 kg of chipped biomass or 1 MJ of bioethanol for the different biomass.

Table S.4. Machinery technical specifications

| Machinery               | Capacity (kg·h\(^{-1}\)) | Mass (kg) | Power (kW) | Diesel consumption | Units                                                                 |
|-------------------------|--------------------------|-----------|------------|--------------------|----------------------------------------------------------------------|
| Truck dumper**          | 13 ton                   | 11,000    | -          | 0.58 l·km\(^{-1}\) | 10                                                                  |
| Wheel loader            | 21,600                   | 30,090    | -          | 90 l·h\(^{-1}\)   | 6                                                                   |
| Chipper                 | 60,000                   | 3,800     | 290        | -                  | 4                                                                   |
| Hopper                  | 64,000                   | 5,000*    | 317        | -                  | (2 units x chipper 1, 2units x chipper 2)                            |
| Disc scalping screen    | 64,000                   | 5,000*    | 7.5        | -                  | 2                                                                   |
| Chip silo + discharge   | 64,000                   | 10,000*   | 7.5        | -                  | 2                                                                   |
| Conveyor belts          | 64,000                   | 5,000*    | 37.5       | -                  | 10 (2 per each conveyor belt)                                       |

*Assumed values, ** 100 km distance transport of feedstock.
Table S.5. Inventory for Storage and chipping area

| Market for electricity, medium voltage (kWh) | Per kg biomass | Per MJ Ethanol |
|-------------------------------------------|----------------|---------------|
|                                           | Eucalyptus globulus | Birch sp. Residues | Spruce sp. Residues | Switchgrass | Miscanthus | Corn Stover | Wheat straw |
|                                           | 0.04            | 0.02          | 0.01              | 0.02          | 0.01       | 0.01        | 0.01         |
| Market for diesel, burned in agricultural machinery (MJ) | 0.31            | 0.11          | 0.10              | 0.11          | 0.05       | 0.05        | 0.05         |
| Market for lubricating oil (kg)            | 2.18·10⁻⁴       | 7.86·10⁻⁶     | 7.14·10⁻⁶         | 7.83·10⁻⁶     | 3.53·10⁻⁶ | 3.58·10⁻⁶ | 3.64·10⁻⁶     |
| Market for agricultural machinery, unspecified (kg) | 1.76·10⁻⁴       | 6.35·10⁻⁶     | 5.77·10⁻⁶         | 6.33·10⁻⁶     | 2.85·10⁻⁶ | 2.89·10⁻⁶ | 2.95·10⁻⁶     | 3.13·10⁻⁶   |
3. Enzyme production area

The enzyme production system was based on the NREL report for cellulase enzyme production (Humbird et al., 2011). This model considers the preparation of a mixture of enzymes, which are catalytic proteins capable to break down cellulose fibers into glucose, cellobiose and soluble glucooligomers. This process area produces cellulase on-site in the biorefinery. Based on the NREL model, the process design considers aerobic fermentation of *Trichoderma reesei*, which is a filamentous fungus capable of secrets high levels of cellulase enzymes when grown in aerobic conditions and the presence of glucose and others cellulase inducers. Table S.6 summarizes the inventory to produce 1 kg of cellulose enzyme. Figure S.3 is a simplified flow diagram of this enzyme production system.

Table S.6. Life cycle inventory for the enzyme production (FU: 1 kg Enzyme) (Humbird et al., 2011)

| Inputs                        | kg   |
|-------------------------------|------|
| Air                           | 2.355|
| Ammonia                       | 0.008|
| CSL                           | 0.012|
| SO$_2$                        | 0.001|
| Glucose                       | 0.206|
| Water                         | 0.825|
| Antifoam                      | 0.001|
| Organic soluble solids        | 0.005|
| Electricity (KW)              | 0.271|

| Outputs (emissions to air)    | kg   |
|-------------------------------|------|
| CO$_2$                        | 0.165|
| Air                           | 2.080|
| Steam                         | 0.053|

Figure S.3. Simplified diagram of cellulase enzyme production area.
4. Inoculum production area

The inoculum production is conducted in a fermenter trains reactor connected in series (Figure S.4) until reaching the inoculum volume required in the fermenter reactors R-301 (assumed as 10% of total volume). The seed production system consists of a set of reactors operating in batch mode (R-302), operating at 32 °C for 24 h batch time. The first train reactor is inoculated with an inoculum from laboratory and its broth is used to inoculate a larger reactor, and so on, until the cell mass is sufficient to inoculate the fermenter reactor (R-301). Table S.7 summarizes the nutrients and electricity required in the reactors R-302 connected in series. Table S.8 gives the reactions and conversion used in the seed fermenter reactors. A high-capacity pump (P-302) is used to transport the inoculum to the reactor R-302.

Figure S.4. Simplified diagram of inoculum production area

Table S.7. Life cycle inventory for the yeast production (FU: 1 kg fermenting bacterium)

| Inputs          | kg  |
|-----------------|-----|
| Air             | 8.5 |
| NH₄Cl           | 0.37|
| NaOH            | 0.23|
| Water           | 30.7|
| Glucose         | 2.0 |
| Electricity (kW)| 0.08|

| Outputs         | kg  |
|-----------------|-----|
| Emissions to water |     |
| Organic compounds dissolved | 33.4 |
| Emissions to air |     |
| Ethanol         | 0.008|
| Steam           | 0.23 |
| CO₂             | 0.9  |
| Air             | 7.7  |

Table S.8. Inoculum seed production reactions and conversions.

| No. | Reaction                                      | Conversion (%) | Limiting reactant |
|-----|-----------------------------------------------|----------------|-------------------|
| 1   | Glucose → 2 ETOH + 2 CO₂                     | 10             | Glucose           |
| 2   | Glucose + 0.865 NH₄Cl + 0.865 NaOH → 5.847 Biomass + 3.07 H₂O + 0.152 CO₂ + 0.8654 NaCl | 60             | Glucose           |
| 3   | Glucose + 6 O₂ → 2 CO₂ + 6 Water             | 30             | Glucose           |

Ref. (Humbird et al., 2011)
5. Yield analysis

a. Pretreatment performance:

Mass balances were determined around pretreatment. The yield for the different pentoses and hexoses sugars released in the pretreatment were calculated as defined in the following equations:

\[
Yield_{\text{glucose, pretreatment}}[\%] = \frac{m_{\text{glucose, pretreatment hydrolyzate}}[\text{kg}]}{m_{\text{theoretical glucose, feedstock}}[\text{kg}]} \cdot 100 \quad \text{Eq. S.3}
\]

Where, the \(m_{\text{glucose, pretreatment hydrolyzate}}\) is the mass of glucose in the recovered pretreated hydrolysate and \(m_{\text{theoretical glucose, feedstock}}\) is the theoretical mass of glucose in the feedstock, calculated by Eq. S.9. The pretreatment yield for other sugars were calculated analogously:

\[
Yield_{\text{mannose, pretreatment}}[\%] = \frac{m_{\text{mannose, pretreatment hydrolyzate}}[\text{kg}]}{m_{\text{theoretical mannose, feedstock}}[\text{kg}]} \cdot 100 \
\[
Yield_{\text{galactose, pretreatment}}[\%] = \frac{m_{\text{galactose, pretreatment hydrolyzate}}[\text{kg}]}{m_{\text{theoretical galactose, feedstock}}[\text{kg}]} \cdot 100 \
\[
Yield_{\text{xylose, pretreatment}}[\%] = \frac{m_{\text{xylose, pretreatment hydrolyzate}}[\text{kg}]}{m_{\text{theoretical xylose, feedstock}}[\text{kg}]} \cdot 100 \
\[
Yield_{\text{arabinose, pretreatment}}[\%] = \frac{m_{\text{arabinose, pretreatment hydrolyzate}}[\text{kg}]}{m_{\text{theoretical arabinose, feedstock}}[\text{kg}]} \cdot 100 \
\[
\text{Eq. S.4} \
\text{Eq. S.5} \
\text{Eq. S.6} \
\text{Eq. S.7}
\]

Thus, the theoretical yield for the pretreatment process is defined as:

\[
Yield_{\text{sugars, PRETREATMENT}} = \frac{\sum m_{\text{sugars, pretreatment hydrolyzate}}[\text{kg}]}{\sum m_{\text{theoretical sugars, feedstock}}[\text{kg}]} \cdot 100 \quad \text{Eq. S.8}
\]

In which, \(m_{\text{theoretical sugars, feedstock}}\) is the sum of theoretical mass of all sugars. Theoretical amounts for hexoses (e.g. glucose, mannose and galactose) were calculated by the equations below:

\[
m_{\text{theoretical glucose, feedstock}}[\text{kg}] = m_{\text{glucan, feedstock}}[\text{kg}] \cdot 1.11 \cdot \left(\frac{180}{162}\right) \quad \text{Eq. S.9}
\]

where, \(m_{\text{glucan, feedstock}}\) is the mass of glucan in the feedstock. The theoretical amount for other sugars were calculated analogously:

\[
m_{\text{theoretical mannose, feedstock}}[\text{kg}] = m_{\text{mannan, feedstock}}[\text{kg}] \cdot 1.11 \cdot \left(\frac{180}{162}\right) \quad \text{Eq. S.10}
\]

\[
m_{\text{theoretical galactose, feedstock}}[\text{kg}] = m_{\text{galactan, feedstock}}[\text{kg}] \cdot 1.11 \cdot \left(\frac{180}{162}\right) \quad \text{Eq. S.11}
\]

and theoretical amounts for pentose (e.g. xylose, arabinose) were calculated as follows:

\[
m_{\text{theoretical xylose, feedstock}}[\text{kg}] = m_{\text{xylan, feedstock}}[\text{kg}] \cdot 1.136 \cdot \left(\frac{150}{132}\right) \quad \text{Eq. S.12}
\]

\[
m_{\text{theoretical arabinose, feedstock}}[\text{kg}] = m_{\text{arabinan, feedstock}}[\text{kg}] \cdot 1.136 \cdot \left(\frac{150}{132}\right) \quad \text{Eq. S.13}
\]

where, 1.11 and 1.136 are the stochiometric values of the pretreatment reactions (see Table 2 in article), 180 is the molecular weight (MW, g·mol\(^{-1}\)) for glucose, mannose and galactose; 162 is the MW for glucan, mannan and galactan; 150 is the MW for xylose and arabinose and 132 is the MW for xylan and arabinan.
The values obtained from process model and pretreatment yield for each feedstock is detailed in Table S.9.

### Table S.9. Sugars balance from process simulation used to determine the pretreatment yield

| m_polymer, pretreatment hydrolyzate (stream 101F) | Eucalyptus | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|-----------------------------------------------|-----------|-----------|-----------|-------------|------------|-------------|-------------|
| Glucose                                      | kg/h      | 1925.4    | 1675.3    | 2173.7      | 3498.5     | 3576.6      | 5063.4      | 4587.3      |
| Xylose                                       | kg/h      | 6609.5    | 13844.1   | 3474.4      | 25942.4    | 23840.9     | 25647.6     | 25684.7     |
| Arabinose                                    | kg/h      | 108.1     | 322.7     | 1226.3      | 1783.7     | 2198.4      | 0.0         | 0.0         |
| Galactose                                    | kg/h      | 364.1     | 246.8     | 912.0       | 568.5      | 688.7       | 0.0         | 0.0         |
| Mannose                                      | kg/h      | 467.5     | 1481.1    | 5211.7      | 341.1      | 108.7       | 0.0         | 0.0         |
| Sum                                          | kg/h      | 9474.6    | 17570.0   | 12998.1     | 32134.1    | 30413.2     | 30711.0     | 30272.0     |

| m_polymer feedstock (stream 102L-G)          |           |           |           |             |            |             |             |
|-----------------------------------------------|-----------|-----------|-----------|-------------|------------|-------------|-------------|
| Glucan                                       | kg/h      | 23995.5   | 20879.0   | 27090.4     | 43600.6    | 44574.8     | 41432.1     | 37536.4     |
| Xylan                                        | kg/h      | 6826.7    | 14299.0   | 3588.6      | 23642.6    | 21727.4     | 22075.4     | 22107.3     |
| Arabinan                                     | kg/h      | 111.7     | 333.3     | 1266.6      | 1535.2     | 1892.2      | 2174.9      | 2763.4      |
| Galactose                                    | kg/h      | 393.3     | 266.6     | 985.1       | 511.7      | 619.8       | 761.2       | 921.1       |
| Mannan                                       | kg/h      | 505.0     | 1599.7    | 5629.2      | 307.0      | 97.9        | 435.0       | 345.4       |

| m_theoretical sugar, feedstock (stream 102L-G) |           |           |           |             |            |             |             |
|-----------------------------------------------|-----------|-----------|-----------|-------------|------------|-------------|-------------|
| Glucose                                       | kg/h      | 29621.1   | 25774.0   | 33441.7     | 53822.5    | 55025.1     | 51145.6     | 46336.6     |
| Xylose                                        | kg/h      | 8812.7    | 18458.8   | 4632.6      | 30520.4    | 28048.1     | 28497.3     | 28538.6     |
| Arabinose                                     | kg/h      | 144.2     | 430.2     | 1635.0      | 1981.8     | 2442.6      | 2807.6      | 3567.3      |
| Galactose                                     | kg/h      | 485.5     | 329.1     | 1216.1      | 631.7      | 765.2       | 939.7       | 1137.1      |
| Mannose                                       | kg/h      | 623.3     | 1974.8    | 6948.9      | 379.0      | 120.8       | 537.0       | 426.4       |
| Sum                                          | kg/h      | 39686.7   | 46966.9   | 47874.2     | 87335.5    | 86401.8     | 83927.1     | 80006.0     |

**Table S.10. Sugars balance from process simulation used to determine the saccharification yield**

| Yield glucose/HYDROLYSIS [%] | Eucalyptus | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|-----------------------------|-----------|-----------|-----------|-------------|------------|-------------|-------------|
|                            | 23.9      | 37.4      | 27.2      | 36.8        | 35.2       | 36.6        | 37.8        |

**b. Saccharification (enzymatic hydrolysis) performance:**

The theoretical glucose yield that can be obtained from the enzymatic cellulose hydrolysis of the pretreated materials is determined according to equation:

\[
Yield_{glucose,HYDROLYSIS} [%] = \frac{m_{glucose\,released,\,enzymatic\,hydrolyzate}[kg]}{m_{theoretical\,glucose,\,pretreatment\,hydrolyzate}[kg]} \cdot 100
\]

Eq. S.14

where \(m_{\,glucose\,released,\,enzymatic\,hydrolyzate}\) is the mass of glucose released during the enzymatic hydrolysis, and \(m_{\,theoretical\,glucose,\,pretreatment\,hydrolyzate}\) is the theoretical mass of glucose content in the glucan recovered in the pretreatment hydrolysate (defined by Eq. S.15). In that way, losses due to glucan degradation in pretreatment biomass are accounted for. Both mass values were directly obtained from the mass balance by using the results from the process simulation, detailed in Table S.10.

\[
m_{\,theoretical\,glucose,\,pretreatment\,hydrolyzate}[kg] = m_{\,glucan,\,pretreatment\,hydrolyzate}[kg] \cdot 1.11 \cdot \left(\frac{180}{162}\right)
\]

Eq. S.15

**Table S.10. Sugars balance from process simulation used to determine the saccharification yield**

| m_glucose, enzymatic hydrolyzate (stream 204L) |              |              |              |              |              |              |              |
|-----------------------------------------------|-------------|-------------|-------------|-------------|--------------|--------------|--------------|
| m_glucose, pretreatment hydrolyzate (stream 120S) | kg/h        | 22360.0     | 19448.96    | 25231.83    | 40611.9      | 41505.8      | 37647.9      |
| m_glucose released, enzymatic hydrolyzate (stream 120S) | kg/h        | 215.7       | 187.57      | 243.35      | 391.7        | 400.3        | 565.5        |
| Yield glucose/HYDROLYSIS [%]                    | 81.1        | 81.1        | 81.1        | 81.1        | 82.9         | 81.04        | 81.04        |

**c. Fermentation performance:**

In order to assess the theoretical amount for ethanol from glucose and xylose consider the next reactions for glucose and xylose fermentation were considered:

\[
\text{Glucose} \rightarrow 2 \text{ETOH} + 2 \text{CO}_2
\]

\[
\text{Xylose} \rightarrow 5/3 \text{ETOH} + 5/3 \text{CO}_2
\]
We can estimate a theoretical amount of ethanol from glucose and xylose, as:

\[
m_{\text{theoretical ethanol, feedstock}}[kg] = m_{\text{theoretical glucose, feedstock}}[kg] \cdot \frac{1}{2} + m_{\text{theoretical xylose, feedstock}}[kg] \cdot \frac{3}{5} \quad \text{Eq. S.16}
\]

Where, \( \frac{1}{2} \) and \( \frac{3}{5} \) are stochiometric factors. Thus, the ethanol yield for the fermentation process can be determined using the equation below:

\[
Yield_{\text{ethanol, FERMENTATION}} \% = \frac{m_{\text{ethanol, fermentation}}[kg]}{m_{\text{theoretical ethanol, feedstock}}[kg]} \cdot 100 \quad \text{Eq. S.17}
\]

Where, \( m_{\text{ethanol, fermentation}} \) is the mass of ethanol obtained in the ethanol plant simulated in Aspen plus, detailed values in Table S.11.

**Table S.11.** Process simulation mass balance used to determine fermentation yield.

|          | Eucalyptus gl. | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|----------|----------------|-----------|-----------|-------------|------------|-------------|-------------|
| \( m_{\text{ethanol, fermentation}} \) (stream 303L) kg/h | 13363.9     | 14676.4   | 13494.3   | 29660.1     | 29284.6    | 28748.4     | 27030.3     |
| \( m_{\text{theoretical ethanol, feedstock}} \) kg/h | 20424.0     | 24245.8   | 19868.2   | 45815.5     | 44946.7    | 43233.8     | 40801.2     |
| Yield_{\text{ethanol, FERMENTATION}} % | 65.4         | 60.5      | 67.9      | 64.7        | 65.2       | 66.5        | 66.2        |
### 6. Carbon ratio

**Table S.12.** Carbon flow (C kmol·h⁻¹) around the bioethanol conversion facility.

| Carbon inputs                  | Eucalyptus gl. | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|--------------------------------|----------------|-----------|-----------|-------------|------------|-------------|-------------|
| Feedstock                      | 25169.7        | 34121.0   | 36450.4   | 48771.0     | 53234.3    | 48061.7     | 51848.2     |
| Yeast                          | 269.7          | 269.7     | 269.7     | 269.7       | 269.7      | 269.7       | 269.7       |
| Enzyme                         | 1.0            | 0.8       | 1.1       | 1.8         | 1.8        | 1.6         | 1.5         |
| CSL                            | 19.7           | 19.7      | 19.7      | 19.7        | 19.7       | 19.7        | 19.7        |
| Total                          | 25460.1        | 34411.3   | 36740.9   | 49062.1     | 53534.3    | 48352.7     | 52139.1     |

**Table S.13.** Ratio to feedstock carbon content (C kmol·C kmol⁻¹ feedstock) around the bioethanol conversion facility.

| Carbon inputs                  | Eucalyptus gl. | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|--------------------------------|----------------|-----------|-----------|-------------|------------|-------------|-------------|
| Feedstock                      | 1.00           | 1.00      | 1.00      | 1.00        | 1.00       | 1.00        | 1.00        |
| Yeast                          | 0.011          | 0.008     | 0.007     | 0.006       | 0.005      | 0.006       | 0.005       |
| Enzyme                         | 3.8·10⁻⁵       | 2.5·10⁻⁵  | 3.0·10⁻⁵  | 3.6·10⁻⁵    | 3.4·10⁻⁵   | 3.4·10⁻⁵    | 2.8·10⁻⁵    |
| CSL                            | 7.8·10⁻⁵       | 5.8·10⁻⁵  | 5.4·10⁻⁵  | 4.0·10⁻⁵    | 3.7·10⁻⁵   | 4.1·10⁻⁵    | 3.8·10⁻⁵    |
| Total                          | 1.01           | 1.01      | 1.01      | 1.01        | 1.01       | 1.01        | 1.01        |

| Carbon outputs                 | Eucalyptus gl. | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|--------------------------------|----------------|-----------|-----------|-------------|------------|-------------|-------------|
| Ethanol                        | 0.27           | 0.22      | 0.19      | 0.31        | 0.28       | 0.31        | 0.27        |
| Combustion exhaust             | 0.57           | 0.56      | 0.65      | 0.51        | 0.51       | 0.50        | 0.50        |
| Ash                            | 0.01           | 0.05      | 0.03      | 0.01        | 0.03       | 0.02        | 0.05        |
| Scrubber vent                  | 0.14           | 0.11      | 0.10      | 0.16        | 0.14       | 0.16        | 0.14        |
| Aerobic gases                  | 0.008          | 0.041     | 0.024     | 0.007       | 0.026      | 0.015       | 0.037       |
| Molecular sieves vent          | 7.5·10⁻⁴       | 4.4·10⁻⁴  | 2.1·10⁻⁴  | 4.7·10⁻⁴    | 7.7·10⁻⁴   | 7.8·10⁻⁴    | 6.3·10⁻⁴    |
| Other emissions not identified  | 0.007          | 0.014     | 0.010     | 0.007       | 0.012      | 0.009       | 0.014       |
| Total                          | 1.01           | 1.01      | 1.01      | 1.01        | 1.01       | 1.01        | 1.01        |
7. Net Energy Value (NEV)

The NEV for the different lignocellulosic feedstocks are presented in Table G.1. The feedstock requirement per MJ of bioethanol is similar for most of the cases (between 2.16 and 2.69 MJ DM-biomass-MJ-1 bioethanol), except for the woody residue’s scenarios, where the values are 3.25 and 3.66 MJ DM-biomass-MJ-1 bioethanol for birch and spruce residues, respectively. The larger amount of biomass required in the case of woody residues is due to its low contents of carbohydrates, which make them require more sugars (and hence biomass) to produce the same quantity of bioethanol of other lignocellulosic feedstocks. Table 5 also summarizes the MJ DM-biomass by MJ-1 bioethanol reported by other studies in the literature, whose values are consistent with the results obtained in our study.

The bioethanol production requires consumption of steam for the pretreatment, bioethanol recovery and wastewater treatment. These process steps demand mid- and high-pressure steam. A high-pressure steam at 320 °C and 13 atm is required in the pretreatment process to reach the temperature and pressure necessary in the dilute-acid reactor (190°C and 12 atm). The recovery area requires mid-pressure steams (4 atm) at 134°C and 144°C for the concentration column and rectification column, respectively. Additionally, a high-pressure steam at 226 °C and 26 atm is used in the 4-effect evaporator system in the wastewater treatment area. In order to perform the energy balance, these steam and power demands must be considered. These internal inputs are supplied by the steam and power produced in the cogeneration area.

The power not used in the processes is considered as a coproduct. The NEV for power are between -0.021 and 0.04 MJ power-MJ-1 bioethanol, which is lower than those reported from other studies, e.g., a corn stover bioethanol production plant has 0.15 MJ power-MJ-1 bioethanol of cogeneration surplus power (Luo et al., 2009), however this study no consider the power required in the biomass preprocessing through chipping. The NEV negative in power for eucalyptus and birch represent an external requirement of electricity in the bioethanol plant.
Table S.14. Energy inputs, energy outputs, and net energy values (NEVs) (all in units of MJ-MJ⁻¹ bioethanol) for the bioethanol production plant for the different feedstocks.

| MJ/MJ bioethanol | Eucalyptus gl. | Birch sp. | N. Spruce | Switchgrass | Miscanthus | Corn stover | Wheat straw |
|------------------|----------------|-----------|-----------|-------------|------------|-------------|-------------|
| **Energy in biomass** |                |           |           |             |            |             |             |
| Feedstock (LHV)  | 2.42           | 3.25      | 3.66      | 2.16        | 2.51       | 2.25        | 2.69        |
| **Energy inputs** |                |           |           |             |            |             |             |
| Heat (as steam) consumption (supplied by Cogeneration area) |                |           |           |             |            |             |             |
| Pretreatment     | 0.23           | 0.21      | 0.23      | 0.10        | 0.11       | 0.11        | 0.12        |
| Bioethanol recovery | 0.29           | 0.42      | 0.60      | 0.37        | 0.38       | 0.33        | 0.36        |
| WWT              | 0.08           | 0.01      | 0.11      | 0.04        | 0.07       | 0.05        | 0.07        |
| **Power consumption (supplied by Cogeneration area)** |                |           |           |             |            |             |             |
| Storage and chipping | 0.06           | 0.05      | 0.06      | 0.03        | 0.03       | 0.03        | 0.03        |
| Pretreatment     | 1.3·10⁻⁴       | 1.5·10⁻⁴  | 2.2·10⁻⁴  | 1.6·10⁻⁴    | 1.7·10⁻⁴   | 1.7·10⁻⁴    | 1.8·10⁻⁴    |
| Saccharification | 9.3·10⁻⁵       | 8.3·10⁻⁵  | 1.2·10⁻⁴  | 7.0·10⁻⁵    | 7.1·10⁻⁵   | 6.9·10⁻⁵    | 6.8·10⁻⁵    |
| Fermentation     | 5.8·10⁻⁴       | 5.4·10⁻⁴  | 7.5·10⁻⁴  | 4.7·10⁻⁴    | 4.7·10⁻⁴   | 4.6·10⁻⁴    | 4.6·10⁻⁴    |
| Cogeneration     | 0.04           | 0.04      | 0.06      | 0.03        | 0.03       | 0.03        | 0.03        |
| WWT              | 0.01           | 0.05      | 0.04      | 0.01        | 0.03       | 0.02        | 0.04        |
| Enzyme production | 3.3·10⁻²       | 2.6·10⁻²  | 3.7·10⁻²  | 2.7·10⁻²    | 2.8·10⁻²   | 2.5·10⁻²    | 2.5·10⁻²    |
| Yeast production | 0.01           | 0.01      | 0.01      | 0.01        | 0.01       | 0.01        | 0.01        |
| **Diesel consumption** |                |           |           |             |            |             |             |
| Storage & Chipping | 0.11           | 0.10      | 0.11      | 0.05        | 0.05       | 0.05        | 0.06        |
| **Energy Outputs** |                |           |           |             |            |             |             |
| Bioethanol (from bioethanol recovery area) | 1.0           | 1.0       | 1.0       | 1.0         | 1.0        | 1.0         | 1.0         |
| Power (from cogeneration area) | 0.13           | 0.18      | 0.24      | 0.11        | 0.13       | 0.12        | 0.14        |
| Heats (as steam, from cogeneration area) | 0.60           | 0.64      | 0.94      | 0.51        | 0.55       | 0.49        | 0.55        |
| **Net energy value (NEV)** |                |           |           |             |            |             |             |
| Net Bioethanol   | 1.0            | 1.0       | 1.0       | 1.0         | 1.0        | 1.0         | 1.0         |
| Net power        | -0.021          | -0.007    | 0.040     | 0.020       | 0.018      | 0.017       | 0.007       |

NOTE: Indirect energy flows, such as transport of feedstocks to the plant and energy required in the chemicals production are not included.
8. Reactions and conversions: Pretreatment, Saccharification and Cofermentation

Table S.15. Pretreatment reactions and conversions

| No. | Reaction                           | Conversion (fraction) | Limiting reactant |
|-----|------------------------------------|-----------------------|-------------------|
|     |                                    | Woody biomass | Grassy biomass | Agricultural residues |                      |
| 1   | Glucan + Water → Glucose           | 0.065        | 0.065        | 0.099               | Glucan              |
| 2   | Glucan + HMF + 2 Water             | -            | -            | 0.003               | Glucan              |
| 3   | Xylan + Water → Xylose             | 0.75         | 0.85         | 0.9                 | Xylan               |
| 4   | Xylan + Water → Xyloolig           | 0.05         | 0.05         | 0.024               | Xylan               |
| 5   | Glucan + Water → Glucoolig         | 0.007        | 0.007        | 0.003               | Glucan              |
| 6   | Xylan → Furfural + 2 Water         | 0.1          | 0.05         | 0.05                | Xylan               |
| 7   | Arabinan → Furfural + 2 Water      | 0.1          | 0.05         | -                   | Arabinan            |
| 8   | Acetate → Acetic                   | 1            | 1            | 1                   | Acetate             |
| 9   | 2 Glucan + Water → Cellobose       | 0.007        | 0.007        | -                   | Glucan              |
| 10  | Galactan + Water → Galactose       | 0.75         | 0.9          | -                   | Galactan            |
| 11  | Mannan + Water → Mannose           | 0.75         | 0.9          | -                   | Mannan              |
| 12  | Galactan → HMF + 2 Water           | 0.15         | 0.05         | -                   | Galactan            |
| 13  | Mannan → HMF + 2 Water             | 0.15         | 0.05         | -                   | Mannan              |
| 14  | Arabinan + Water → Arabinose       | 0.75         | 0.9          | -                   | Arabinan            |

Ref. (Wooley et al., 1999) (Laser et al., 2009) (Humbird et al., 2011)

Table S.16. Saccharification and cofermentation reactions and conversion efficiencies

| No. | Reaction                           | Conversion (fraction) | Limiting reactant |
|-----|------------------------------------|-----------------------|-------------------|
|     |                                    | Woody biomass | Grassy biomass | Agricultural residues |                      |
|     | **SACCHARIFICATION**               |                      |                  |                      |                      |
| 1   | Glucan + Water → Glucose           | 0.90          |               | Glucan              |
| 2   | 2 Glucan + Water → Cellobose       | 0.012         |               | Glucan              |
| 3   | Cellobose → Glucose                | 1.00          |               | Cellobose           |
| 4   | Glucan → Gluco-oligomers           | 0.04          |               | Glucan              |
|     | **COFERMENTATION**                 |                      |                  |                      |                      |
| 1   | Glucose → 2 ETOH + 2 CO₂           | 0.95          |               | Glucose             |
| 2   | Glucose + 0.047 CSL + 0.018 DAP → 6 Biomass + 2.4 H₂O | 0.002 | Glucose |
| 3   | Glucose + 2 H₂O → 2 Glycerol + O₂  | 0.004         |               | Glucose             |
| 4   | Glucose + 2 CO₂ → 2 Succinic acid + O₂ | 0.006       | Glucose |
| 5   | 3 Xylose → 5 ETOH + 5 CO₂          | 0.85          |               | Xylose              |
| 6   | Xylose + 0.039 CSL + 0.015 DAP → 5 Biomass + 2 H₂O | 0.019       | Xylose |
| 7   | Xylose + 5 H₂O → 5 Glycerol + 2.5 H₂O | 0.003   | Xylose |
| 8   | Xylose + H₂O → Xylitol + 0.5 H₂O  | 0.046         |               | Xylose              |
| 9   | 3 Xylose + 5 CO₂ → 5 Succinic acid + 2.5 H₂O | 0.009   | Xylose |
|     | Ref. (Humbird et al., 2011)        |                      |                  |                      |                      |
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