Data Article

Life cycle inventory data for ethyl levulinate production from Colombian rice straw

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**Keywords:**
Biomass
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**Abstract**

This data article is associated with the research article “Sustainable production of ethyl levulinate by levulinic acid esterification obtained from Colombian rice straw”. This paper shows the methodology to calculate the Life Cycle Inventory (LCI) of the foreground system to perform the Life Cycle Assessment (LCA) of the ethyl levulinate (EL) production from Colombian rice straw (RS). This process encompasses two main stages: (i) RS production (involving cultivation and harvesting) and (ii) EL production (involving acid hydrolysis, levulinic acid (LA) purification, and EL production). On one hand, foreground data related to paddy rice cultivation was gathered from the literature review. Besides, emissions of the cultivation stage were calculated using the IPCC (Intergovernmental Panel on Climate Change) methodology. The SQCB (Sustainable Quick Check for Biofuels) methodology was used to calculate NH₃, NOₓ, N₂O and NO₂ emissions, whereas the SALCA (Swiss Agricultural Life Cycle Assessment) model was used to calculate phosphorous emissions to water. The Turc method was employed to calculate the irrigation requirements based on the rainfall and agrological features of rice culture. On the other hand, foreground data related to RS conversion to EL within a biorefinery scheme was obtained from simulation using Aspen Plus v.12. Lastly, background data associated with raw materials, catalysts, and utilities were gathered from Ecoinvent database. All the inventories are meaningful to carry out future environmental

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assessments involving sustainable production processes using RS as raw material or biorefinery processes using dilute acid hydrolysis.

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### Specifications Table

| Subject                  | Chemical Engineering: Process Chemistry and Technology |
|--------------------------|-------------------------------------------------------|
| Specific subject area    | Life Cycle Inventory and Chemical Process Simulation |
| Type of data             | Table and Figure                                      |
| How data were acquired   | The foreground data was acquired from process simulation using Aspen Plus v.12 (Aspen Tech, MA, USA) and Aspen Economic Analyzer v.12 (Aspen Tech, MA, USA). The background data was gathered from Ecoinvent v.3.4 and the literature review for data related to rice cultivation. |
| Data format              | Raw and processed                                     |
| Description of data collection | Primary data concerning mass and energy balance to produce ethyl levulinate from Colombian rice straw was obtained from the literature review, Aspen Plus simulations, databases such as Ecoinvent version 3.4, scientific reports and academic theses. Data for paddy rice cultivation was obtained from literature review and calculations using methods which are described along this document. |
| Data source location     | Universidad de La Sabana                             |
|                         | City/Town/Region: Chía, Cundinamarca                 |
| Country                 | Colombia                                              |
| Data accessibility       | Raw data                                              |
| Repository name          | Ethyl_levulinate_from_Colombian_Rice_Straw           |
| DOI                     | 10.17632/p4prb8mb32.1                                 |
| Related research article | C. Cañon, N. Sanchez, M. Cobo, Sustainable production of ethyl levulinate by levulinic acid esterification obtained from Colombian rice straw, J. Clean. Prod., 377 (2022) 134276. |
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### Value of the Data

- The data shown in this contribution support the Life Cycle Assessment depicted in the main article. This manuscript presents information that were not included in a explicit way in the related research article such as details of the process simulations performed, sensitivity analysis for distillation columns, paddy rice culture inventory calculation, and contribution analysis impact categories assessed.
- The data shown in this document could be used by anyone who wants to assess the environmental performance of the e-fuels and bioproducts production derived from Colombian rice straw.
- These data could be used as input in other Life Cycle Assessment studies and for simulate similar processes such as the production of other bio-products (e.g., gamma-valerolactone, furfuryl alcohol, furanic compounds, other levulinate esters, among others) derived from rice straw, and other Life Cycle Assessments that consider rice straw as raw material.

### 1. Objective

The data presented in this data article is generated as a result of the techno-economic and environmental assessment performed to evaluate the preliminary feasibility for the production of ethyl levulinate from Colombian rice straw. This data is mainly focused on two aspects. First,
Table 1
Data collection for the construction of the LCI in each stage of the product system.

| Process stage       | Methodology                              |
|---------------------|------------------------------------------|
| Biomass cultivation | Ecoinvent                                 |
| Biomass harvesting  | Literature review                         |
| Acid Hydrolysis     | Ecoinvent                                 |
| Solid Combustion    | Literature review                         |
| LA purification     | Process simulation in Aspen Plus         |
| EL production       |                                          |

Table 2
Proximate analysis of rice and carbon content on each fraction.

| Analysis     | Unit          | Value   | g C/kg |
|--------------|---------------|---------|--------|
| Crude protein| % Dry matter  | 14.2    | 530    |
| Crude Fiber  | % Dry matter  | 4.10    | 440    |
| NDF          | % Dry matter  | 12.4    | 440    |
| ADF          | % Dry matter  | 3.2     | 440    |
| Lignin       | % Dry matter  | 1.2     | 645    |
| Lipids       | % Dry matter  | 13.2    | 750    |
| Starch       | % Dry matter  | 42.0    | 440    |
| Total sugars | % Dry matter  | 3.8     | 440    |

NDF: Neutral detergent fiber; ADF: acid detergent fiber.

The description of the simulation process performed in Aspen Plus v12 (AspenTech, Bedford, MA, USA) as well as the mass and energy balance obtained for the overall process. Second, the life cycle inventory obtained from the simulation process and the literature review for the paddy rice cultivation in Colombian context and the subsequent biorefinery process. This Life Cycle Assessment was performed in OpenLCA v1.10 (GreenDelta, Berlin, Germany). Economic data for the process economic assessment is included in this data article. The detailed life cycle inventories presented in this article support the main article discussion about environmental impacts related to the production of ethyl levulinate from rice straw and the identification of improvement opportunities for the process under study. Likewise, this inventory data could be used for further research related to the valorization of agro-industrial residues in the Colombian context.

2. Data Description

This article shows the Life Cycle Inventory (LCI) of the foreground system needed to perform a Life Cycle Assessment (LCA) of the production of ethyl levulinate (EL) from Colombian rice straw (RS). These data give transparency to the main results shown in the reference article [1]. LCI was gathered from process simulation using Aspen Plus v12 (AspenTech, Bedford, USA), Ecoinvent database v.3.4, scientific, academic reports, and websites. Table 2 shows the data collection sources for the LCI construction. Table 1 shows the proximate analysis of RS coming from the Orinoquia Region (Colombia). Table 3 depicts the LCI of the paddy rice cultivation stage. Fig. 1 presents the main flowsheet associated with the conversion of RS into EL. Herein, five hierarchy blocks were employed. Fig. 2 shows the flowsheet for the ACID-HYD block that represents the hydrolysis of RS. Fig. 3 shows the detailed purification (HYD-SEP, in Fig. 1) of LA and furfural (FFR). Fig. 4 shows the detailed purification of FFR (FFR-SEP, in Fig. 1). Fig. 5 depicts the ESTERIF block that simulated the esterification of LA with ethanol to produce EL and its subsequent purification through a separation train. Lastly, Fig. 6 portrays the combustion of solid waste to produce low pressure steam (LPS) and medium pressure steam (MPS). Detailed information of subroutines for the aforementioned process is described in Tables 4 and 5. Table 6 presents the list of all reactions used for the RStoics units. Table 7 shows the operating conditions for the
Fig. 1. Simulation process in Aspen Plus (alternative scenario).

Fig. 2. ACID-HYD Hierarchy block details for EL production from RS. This flowsheet includes the two step acid hydrolysis of RS, acid neutralization and solids separation from liquid hydrolyzed.; M: MHeaTX; MX: mixer; HS: heat splitter; HT: heater; P: pump; RS: RStoic; SS: solid separator; VAL: valve.
Table 3
Life Cycle Inventory for rice culture in Orinoquia region in Colombia.

| Component                        | Stream type | Unit | Amount       |
|----------------------------------|-------------|------|--------------|
| Paddy rice                       | Output      | kg   | 1000.000     |
| Rice Straw                       | Output      | kg   | 1400.000     |
| Land                             | Input       | ha   | 0.201        |
| Ammonia                          | Input       | kg   | 104.340      |
| P₂O₅                             | Input       | kg   | 7.243        |
| K₂O                              | Input       | kg   | 31.590       |
| Diesel                           | Input       | L    | 25.1         |
| Irrigation                       | Input       | m³   | 1047.561     |
| Water (rain)                     | Input       | m³   | 2879.276     |
| CO₂ (capture)                    | Emission to air | kg | 0.032 |
| Nitrogen oxides                  | Emission to air | kg | 0.040 |
| Particulate Matter               | Emission to air | kg | 0.040 |
| CO                               | Emission to air | kg | 0.317 |
| CO₂                              | Emission to air | kg | 74.761 |
| NH₃                              | Emission to air | kg | 0.806 |
| NO₂                              | Emission to air | kg | 0.872 |
| N₂O                             | Emission to air | kg | 0.461 |
| CH₄                              | Emission to air | kg | 16.711 |
| Nitrates                         | Emission to water | kg | 36.937 |
| Phosphate to surface water       | Emission to water | kg | 0.055 |

Fig. 3. HYD-SEP Hierarchy block details for EL production from RS. This flowsheet includes a two-step flash evaporation for remove water and FFR from the hydrolyzed stream, sugar recovery and a distillation for LA purification. FL: flash; FS: flow splitter; MX: mixer; HT: heater; P: pump; RF: RadFrac; SEP: sep-2; VAL: valve.

Five distillation units. Sensitivity analysis of these distillation columns is briefly shown in Fig. 7 (RF-110), Fig. 8 (RF-201), Fig. 9 (RF-202), Fig. 10 (RF-301), and Fig. 11 (RF-302).

Two scenarios were assessed. On one hand, a base scenario without the combustion of solid hydrolysed residue corresponding to the hierarchy block HEAT-GEN (Fig. 6) and using a paddy rice yield of 4.95 t/ha. The mass and energy balance for base scenario are presented in Table 8. LCI of the base scenario is presented in Table 9. The contribution analysis performed for the base scenario is presented in Fig. 12. On the other hand, the alternative scenario includes the combustion of solid waste along with an increment of the paddy rice yield to 5.7 t/ha. The mass and energy balance for the alternative scenario is presented Table 10. LCI for alternative scenario
Table 4
Description of main subroutines to produce ethyl levulinate from rice straw.

| Hierarchy block | Aspen subroutine | Description | Conditions | Assumptions |
|-----------------|------------------|-------------|------------|-------------|
| ACID-HYD        | RS-101           | Reactor for the first stage of dilute acid hydrolysis | T: 210°C  
  P: 20 bar  
  Reactions: reactions 1 to 5 in Table 6  
  Utility: cooling air  
  Q: -12,029.3 MJ/h | Stoichiometric reactions.  
  No reversible reactions |
| ACID-HYD        | RS-102           | Reactor for the second stage of dilute acid hydrolysis | T: 190°C  
  P: 18 bar  
  Reactions: reactions 6 to 8 in Table 6  
  Utility: cooling air  
  Q: -418.7 MJ/h | Stoichiometric reactions.  
  No reversible reactions |
| ACID-HYD        | RS-103           | Reactor for sulfuric acid neutralization with sodium hydroxide | T: 70°C  
  P: 6 bar  
  Reactions: reaction 17 in Table 6  
  Utility: cooling air  
  Q: -2,300.1 MJ/h | Stoichiometric reactions.  
  No reversible reactions |
| ACID-HYD        | H101             | Heat exchanger for preheating of hydrolysis water | Out temperature of cold stream 185°C  
  Temperature difference: 10°C | Geometry and rigorous design avoided |
| ACID-HYD        | SS-101           | Solid separator for solid hydrolyzed separation from liquid hydrolyzed stream | T: 70°C  
  P: 6 bar  
  Fraction of solids to solid outlet: 0.999  
  Fraction of liquid to liquid outlet: 0.99 | No particle size distribution |
| ACID-HYD        | SS-102           | Solid separator for sodium sulfate separation from liquid hydrolyzed stream | T: 70°C  
  P: 6 bar  
  Fraction of solids to solid outlet: 0.99999  
  Fraction of liquid to liquid outlet: 0.9999 | No particle size distribution |
| ACID-HYD        | P-101            | Pump for water make up for dilute acid hydrolysis | P out: 20 bar  
  Efficiency: 70%  
  Utility: electricity | Only liquid phase |
| ACID-HYD        | HT-101-H         | Heat exchanger for hydrolysis water preheating | P: 20 bar  
  Utility: HPS  
  Outlet temperature: 212.8°C  
  Outlet vapor fraction: 0.57  
  Q: 8420.1 MJ/h | No pressure drop considered |
| ACID-HYD        | HT-102-H         | Heat exchanger for hydrolysis water evaporation | P: 20 bar  
  Utility: HPS  
  Outlet temperature: 215°C  
  Outlet vapor fraction: 0.999  
  Q: 5,651.2 MJ/h | No pressure drop considered |
| ACID-HYD        | HT-103-H         | Heat exchanger for cooling hydrolysate stream from RS-101 to RS-102 | Outlet temperature: 190°C  
  P: 18 bar  
  Utility: Cooling air  
  Q: -797.3 MJ/h | No pressure drop considered |
| ACID-HYD        | VAL-102          | Valve for pressure reduction of hydrolysate stream | Outlet pressure: 6 bar  
  Valid phases: liquid and vapor | Adiabatic |
| ACID-HYD        | HT-104-C         | Heat exchanger for hydrolysate stream cooling previous to neutralization | Outlet temperature: 70°C  
  P: 6 bar  
  Utility: Cooling air  
  Q: -9,163.5 MJ/h | No pressure drop considered |
| HYD-SEP         | FL-110           | First flash unit for LA and FFR separation from liquid hydrolyzed stream | Pressure drop: 0 bar | Adiabatic |
| HYD-SEP         | FL-111           | Second flash unit for LA and FFR separation from liquid hydrolyzed stream | Pressure drop: 0 bar | Adiabatic |

(continued on next page)
| Hierarchy block | Aspen subroutine | Description | Conditions | Assumptions |
|-----------------|------------------|-------------|------------|-------------|
| HYD-SEP         | SEP-110          | Separation unit for unreacted sugar recovery | Split fraction for fructose: 0.9999<br>Split fraction for xylose: 0.9999<br>Split fraction for water: 0.2<br>P: 1.2 bar | Non-rigorous unit |
| HYD-SEP         | RF-110           | Distillation column for levulinic acid purification | NS: 14<br>FS: 6 (above)<br>Molar reflux ratio: 0.7<br>Bottoms to feed ratio: 0.68<br>Convergence: strongly non-ideal liquid<br>Condenser pressure: 0.2 bar<br>Column pressure dop: 0.25 bar<br>Murphree efficiency: 65%<br>Condenser utility: cooling water<br>Condenser Q: -62.4 MJ/h<br>Reboiler utility: HPS<br>Reboiler Q: 89.6 MJ/h | Internal design not considered |
| HYD-SEP         | VAL-110          | Valve for pressure drop required to FL-110 unit | Outlet pressure: 1.75 bar | Adiabatic |
| HYD-SEP         | VAL-111          | Valve for pressure drop required to FL-111 unit | Outlet pressure: 1 bar | Adiabatic |
| HYD-SEP         | VAL-112          | Valve for pressure drop required to RF-110 unit | Outlet pressure: 0.3 bar | Adiabatic |
| HYD-SEP         | HT-110-H         | Heat exchanger for heating requirement for FL-110 unit | Outlet temperature: 134°C<br>P: 3 bar<br>Utility: MPS<br>Q: 9,723.6 MJ/h | No pressure drop considered |
| HYD-SEP         | HT-111-C         | Heat exchanger for cooling vapor stream from FL-110 unit | Outlet vapor fraction: 0.12<br>Pressure drop: 0 bar<br>Q: -7971.6 MJ/h | No utility required |
| HYD-SEP         | HT-112-H         | Heat exchanger for heating requirement for FL-111 unit | Outlet temperature: 125°C<br>Pressure drop: 0 bar<br>Q: 46.19 MJ/h | No utility required |
| FFR-SEP         | M201             | Heat exchanger for heat integration of liquid stream feed to furfural azeotropic distillation | Cold stream outlet temperature: 102°C | No pressure drop considered |
| FFR-SEP         | RF-201           | Distillation column for azeotropic distillation of furfural from water | NS: 30<br>FS: 2 (above)<br>Molar reflux ratio: 1.7<br>Distillate to feed ratio: 0.1<br>Convergence: azeotropic<br>Condenser pressure: 1 bar<br>Column pressure dop: 0.4 bar<br>Murphree efficiency: 65%<br>Condenser utility: cooling water<br>Condenser Q: -5,160.6 MJ/h<br>Reboiler utility: LPS<br>Reboiler Q: 5,513.3 MJ/h | Internal design not considered |
| FFR-SEP         | RF-202           | Distillation column for furfural purification | NS: 12<br>FS: 6 (above)<br>Molar reflux ratio: 0.5<br>Bottoms to feed ratio: 0.8<br>Convergence: standard<br>Condenser pressure: 1 bar<br>Column pressure dop: 0.3 bar<br>Murphree efficiency: 65%<br>Condenser utility: cooling water<br>Condenser Q: -35.8 MJ/h<br>Reboiler utility: HPS<br>Reboiler Q: 57.8 MJ/h | Internal design not considered |

(continued on next page)
| Hierarchy block | Aspen subroutine | Description | Conditions | Assumptions |
|----------------|-----------------|-------------|------------|-------------|
| FFR-SEP        | HT-201-C        | Heat exchanger for cooling of liquid stream feed to furfural azeotropic distillation | Outlet temperature: 99°C Outlet pressure: 1.02 bar Utility: cooling air Q: -994.5 MJ/h | No pressure drop considered |
| FFR-SEP        | HT-202-C        | Heat exchanger for cooling of distillate stream from RF-201 unit to DC-201 unit | Outlet temperature: 60°C Outlet pressure: 1 bar Utility: cooling water Q: -164.5 MJ/h | No pressure drop considered |
| FFR-SEP        | HT-203-H        | Heat exchanger for heating requirement for RF-202 unit | Outlet temperature: 96°C Outlet pressure: 1.16 bar Utility: LPS Q: 16.4 MJ/h | No pressure drop considered |
| FFR-SEP        | HT-204-C        | Heat exchanger for cooling of furfural product stream | Outlet temperature: 38°C Outlet pressure: 1 bar Utility: cooling air Q: -50.5 MJ/h | No pressure drop considered |
| FFR-SEP        | P-201           | Pump for pressure adjust required for DC-201 unit | P out: 1.3 bar Efficiency: 70% Utility: electricity | Only liquid phase |
| FFR-SEP        | P-303           | Pump for water recycle for dilute acid hydrolysis | P out: 20 bar Efficiency: 70% Utility: electricity | Only liquid phase |
| FFR-SEP        | DC-201          | Decanter unit for furfural rich phase separation from distillate stream from RF-201 | T: 60°C P: 1.3 bar Key components for separation: water and furfural | - |
| ESTERIF        | RS-301          | Esterification reactor | T: 120°C P: 4.5 bar Reactions: 9 reaction in Table 6 Utility: MPS Q: 9.1 MJ/h | Stoichiometric reactions. No reversible reactions |
| ESTERIF        | RF-301          | Distillation column for water and ethanol separation from esterification reaction outlet stream | NS: 10 FS: 6 (above) Molar reflux ratio: 0.5 Bottoms to feed ratio: 0.11 Convergence: Strongly non-ideal liquid Condenser pressure: 1 bar Column pressure dop: 0.3 bar Murphee efficiency: 65% Condenser utility: cooling water Condenser Q: -905.1 MJ/h Reboiler utility: HPS Reboiler Q: 850.8 MJ/h | Internal design not considered |
| ESTERIF        | RF-302          | Distillation column for ethyl levulinate purification | NS: 19 FS: 8 (above) Molar reflux ratio: 0.8 Distillate to feed ratio: 0.85 Convergence: Strongly non-ideal liquid Condenser pressure: 0.2 bar Column pressure dop: 0.25 bar Murphee efficiency: 65% Condenser utility: cooling water Condenser Q: -149.9 MJ/h Reboiler utility: HPS Reboiler Q: 115.1 MJ/h | Internal design not considered |
| ESTERIF        | SEP-301         | Molecular sieve separation for ethanol recycling | Split fraction for water: 0.0001 Split fraction for ethanol: 0.996 Split fraction for levulinic acid: 0.0001 Split fraction for ethyl levulinate: 0.0001 P: 1.5 bar | Non-rigorous unit |

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Table 4 (continued)

| Hierarchy block | Aspen subroutine | Description | Conditions | Assumptions |
|-----------------|------------------|-------------|-----------|-------------|
| ESTERIF         | VAL-301          | Valve for pressure drop required to RF-301 unit | Outlet pressure: 1.16 bar | Adiabatic |
| ESTERIF         | VAL-302          | Valve for pressure drop required to RF-302 unit | Outlet pressure: 0.4 bar | Adiabatic |
| ESTERIF         | P-301            | Pump for levulinic acid stream pressure adjust required for esterification reaction | P out: 4.5 bar Efficiency: 70% Utility: electricity | Only liquid phase |
| ESTERIF         | P-302            | Pump for ethanol stream pressure adjust required for esterification reaction | P out: 4.5 bar Efficiency: 70% Utility: electricity | Only liquid phase |
| ESTERIF         | P-303            | Pump for pressure adjust of distillate stream from RF-301 to SEP-301 | P out: 1.5 bar Efficiency: 70% Utility: electricity | Only liquid phase |
| ESTERIF         | HT-301-H         | Heat exchanger for levulinic acid stream cooling | Outlet temperature: 120°C Outlet pressure: 4.5 bar Utility: cooling air Q: -57.2 MJ/h | No pressure drop considered |
| ESTERIF         | HT-302-H         | Heat exchanger for ethanol stream heating required for esterification reaction | Outlet temperature: 120°C Outlet pressure: 4.5 bar Utility: MPS Q: 163.3 MJ/h | No pressure drop considered |
| ESTERIF         | HT-304-C         | Heat exchanger for cooling of distillate stream from RF-301 to SEP-301 | Outlet temperature: 50°C Outlet pressure: 1.5 bar Utility: cooling air Q: -55.9 MJ/h | No pressure drop considered |
| ESTERIF         | HT-305-C         | Heat exchanger for cooling of ethyl levulinate product stream | Outlet temperature: 28°C Outlet pressure: 1 bar Utility: cooling water Q: -51.7 MJ/h | No pressure drop considered |
| HEAT-GEN        | RS-401           | Reactor for solid hydrolyzed stream combustion | T: 904°C P: 10 bar Reactions: 10 to 16 reactions in Table 6 | Stoichiometric reactions. No reversible reactions. Complete combustion Adiabatic reactor. Excess air to temperature control. |
| HEAT-GEN        | SEP-401          | Separation of ashes from combustion reactor | Split fraction for solid components: 0.0001 Split fraction for other components: 0.9999 | No pressure drop considered |
| HEAT-GEN        | M401             | Heat exchanger that simulates furnace of steam generation cycle | Hot stream outlet temperature: 40°C Hot stream outlet pressure: 10 bar Cold stream outlet temperature: 5 bar | No pressure drop considered |
| HEAT-GEN        | HT-401-H         | Heat exchanger for combustion air preheating | Outlet temperature: 110°C Outlet pressure: 10 bar Utility: MPS Q: 1106.6 MJ/h | No pressure drop considered |
| HEAT-GEN        | HT-402-C         | Heat exchanger that simulates the condensing of generated MPS used in the overall process | Outlet temperature: 174°C Outlet vapor fraction: 0 Utility: none Q: -5.181MJ/h | No pressure drop considered |
| HEAT-GEN        | HT-403-C         | Heat exchanger that simulates the condensing of generated LPS used in the overall process | Outlet temperature: 124°C Outlet vapor pressure: 0 Utility: none Q: -6.810MJ/h | No pressure drop considered |
| HEAT-GEN        | HT-404-C         | Heat exchanger that simulates condenser of steam generation cycle | Outlet temperature: 30°C Outlet vapor fraction: 0 Utility: cooling air Q: -2.750.9 MJ/h | No pressure drop considered |

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Table 4 (continued)

| Hierarchy block | Aspen subroutine | Description | Conditions | Assumptions |
|-----------------|------------------|-------------|------------|-------------|
| HEAT-GEN        | P-402            | Pump for water pressurization for steam generation | P out: 5 bar<br>Efficiency: 70%<br>Utility: electricity | Only liquid phase |
| HEAT-GEN        | TUR-401          | Turbine for MPS generation | Discharge pressure: 3.7 bar<br>Isentropic efficiency: 80%<br>Mechanical efficiency: 80%<br>Isentropic using GPSA method |  |
| HEAT-GEN        | TUR-402          | Turbine for LPS generation | Discharge pressure: 1.95 bar<br>Isentropic efficiency: 80%<br>Mechanical efficiency: 80%<br>Isentropic using GPSA method |  |

T: temperature; P: pressure; FS: feed stage; NS: number of stages; Q: net duty; LPS: low pressure steam; MPS: medium pressure steam.

Fig. 4. FFR-SEP Hierarchy block details for EL production from RS. This flowsheet includes the two step distillation of FFR with a decanter unit. DC: decanter; FS: flow splitter; M: MHeatX; MX: mixer; HT: heater; P: pump; RF: RadFrac.

Fig. 5. ESTERIF Hierarchy block details for EL production from RS. This flowsheet includes the esterification reaction, two step distillation for EL and LA purification, and ethanol recovery. FS: flow splitter; MX: mixer; HT: heater; P: pump; RF: RadFrac; RS: RStoic; SEP: sep-2; VAL: valve.
| Hierarchy block | Subroutine | Purpose |
|-----------------|------------|---------|
| ACID-HYD        | RS-101     | Reactor for the first stage of dilute acid hydrolysis using sulfuric acid |
| ACID-HYD        | RS-102     | Reactor for the second stage of dilute acid hydrolysis using sulfuric aid |
| ACID-HYD        | RS-103     | Reactor for sulfuric acid neutralization with sodium hydroxide |
| ACID-HYD        | H101       | Heat exchanger for preheating hydrolysates water using heat integration of hydrolysed outlet stream (liquid and solid) and the hydrolysis water (includes make-up water and recycled water from FFR distillation) |
| ACID-HYD        | SS-101     | Solid separator for solid hydrolyzed separation from hydrolyzed outlet stream |
| ACID-HYD        | SS-102     | Solid separator for sodium sulfate separation from liquid hydrolyzed stream from SS-101 |
| ACID-HYD        | P-101      | Pump for water make up for dilute acid hydrolysis |
| ACID-HYD        | HT-101-H   | Heat exchanger for hydrolysis water preheating |
| ACID-HYD        | HT-102-H   | Heat exchanger for hydrolysis water evaporation |
| ACID-HYD        | HT-103-H   | Heat exchanger for cooling hydrolysate stream from RS-101 to RS-102 |
| ACID-HYD        | VAL-102    | Valve for pressure reduction of hydrolysate stream |
| ACID-HYD        | HT-104-C   | Heat exchanger for hydrolysate stream cooling previous to neutralization |
| HYD-SEP         | FL-110     | First flash unit for LA and FFR separation from liquid hydrolyzed stream |
| HYD-SEP         | FL-111     | Second flash unit for LA and FFR separation from liquid hydrolyzed stream |
| HYD-SEP         | SEP-110    | Separation unit for unreacted sugars recovery |
| HYD-SEP         | RF-110     | Distillation column for levulinic acid purification |
| HYD-SEP         | VAL-110    | Valve for pressure drop required to FL-110 unit |
| HYD-SEP         | VAL-111    | Valve for pressure drop required to FL-111 unit |
| HYD-SEP         | VAL-112    | Valve for pressure drop required to RF-110 unit |
| HYD-SEP         | HT-110-H   | Heat exchanger for heating requirement for FL-110 unit |
| HYD-SEP         | HT-111-C   | Heat exchanger for cooling vapor stream from FL-110 unit |
| HYD-SEP         | HT-112-H   | Heat exchanger for heating requirement for FL-111 unit |
| FFR-SEP         | M201       | Heat exchanger for heat integration of liquid stream feed to furfural azeotropic distillation |
| FFR-SEP         | RF-201     | Distillation column for azeotropic distillation of furfural from water |
| FFR-SEP         | RF-202     | Distillation column for furfural purification |
| FFR-SEP         | HT-201-C   | Heat exchanger for cooling of liquid stream feed to furfural azeotropic distillation |
| FFR-SEP         | HT-202-C   | Heat exchanger for cooling of distillate stream from RF-201 unit to DC-201 unit |
| FFR-SEP         | HT-203-H   | Heat exchanger for heating requirement for RF-202 unit |
| FFR-SEP         | HT-204-C   | Heat exchanger for cooling of furfural product stream |
| FFR-SEP         | P-201      | Pump for pressure adjust required for DC-201 unit |
| FFR-SEP         | P-303      | Pump for water recycle for dilute acid hydrolysis |
| FFR-SEP         | DC-201     | Decanter unit for furfural rich phase separation from distillate stream from RF-201 |
| ESTERIF         | RS-301     | Esterification reactor using ethanol as solvent and as esterification reagent |
| ESTERIF         | RF-301     | Distillation column for water and ethanol separation from esterification reaction outlet stream |
| ESTERIF         | RF-302     | Distillation column for EL and LA purification |
| ESTERIF         | SEP-301    | Molecular sieve separation for ethanol recycling |
| ESTERIF         | VAL-301    | Valve for pressure drop required to RF-301 unit |
| ESTERIF         | VAL-302    | Valve for pressure drop required to RF-302 unit |
| ESTERIF         | P-301      | Pump for levulinic acid stream pressure adjust required for esterification reaction |
| ESTERIF         | P-302      | Pump for ethanol stream pressure adjust required for esterification reaction |
| ESTERIF         | P-303      | Pump for pressure adjust of distillate stream from RF-301 to SEP-301 |
| ESTERIF         | HT-301-H   | Heat exchanger for levulinic acid stream cooling required for esterification reaction |
| ESTERIF         | HT-302-H   | Heat exchanger for ethanol stream heating required for esterification reaction |
| ESTERIF         | HT-304-C   | Heat exchanger for cooling of distillate stream from RF-301 to SEP-301 |
| ESTERIF         | HT-305-C   | Heat exchanger for cooling of ethyl levulinate product stream |
| HEAT-GEN        | RS-401     | Reactor for solid hydrolyzed stream combustion, assuming complete combustion and excess air to temperature control |
| HEAT-GEN        | SEP-401    | Separation of ashes from combustion reactor |
| HEAT-GEN        | M401       | Heat exchanger that simulates furnace of steam generation cycle |
| HEAT-GEN        | HT-401-H   | Heat exchanger for combustion air preheating |
| HEAT-GEN        | HT-402-C   | Heat exchanger that simulates the condensing of generated MPS used in the overall process |
| HEAT-GEN        | HT-403-C   | Heat exchanger that simulates the condensing of generated LPS used in the overall process |
| HEAT-GEN        | HT-404-C   | Heat exchanger that simulates condenser of steam generation cycle |
| HEAT-GEN        | P-402      | Pump for water pressurization for steam generation |
| HEAT-GEN        | TUR-401    | Turbine for MPS generation |
| HEAT-GEN        | TUR-402    | Turbine for LPS generation |
Fig. 6. HEAT-GEN Hierarchy block details for EL production from RS including Heat Generation. This flowsheet includes the combustion of solid hydrolyzed and a Rankine cycle for LPS and MPS generation. FS: flow splitter; HT: heater; M: MHeatX; MX: mixer; P: pump; S: RF: RadFrac; SEP: sep-2; TUR: turbine; VAL: valve.

Table 6
Reactions involved in the EL production from rice straw.

| # | Reaction                                      | Fractional conversion | Temperature(°C) | Pressure(Bar) |
|---|----------------------------------------------|-----------------------|-----------------|---------------|
| 1 | Cellulose + H₂O → Fructose                   | 0.65                  | 210             | 20            |
| 2 | Hemicellulose + H₂O → Xylose                 | 0.82                  | 210             | 20            |
| 3 | Hemicellulose + H₂O → 2.5 AA                 | 0.05                  | 210             | 20            |
| 4 | Fructose → Humins + H₂O                      | 0.1                   | 210             | 20            |
| 5 | Xylose → Humins + H₂O                        | 0.1                   | 210             | 20            |
| 6 | Xylose → Furfural + 3H₂O                     | 0.80                  | 190             | 18            |
| 7 | Fructose → HMF + 3H₂O                        | 0.70                  | 190             | 18            |
| 8 | HMF + 2H₂O → LA + FA                        | 0.999                 | 190             | 18            |
| 9 | LA + Ethanol → EL + H₂O                      | 0.85                  | 120             | 4.5           |
| 10| Cellulose + 6 O₂ → 5 H₂O + 6 CO₂             | 0.999                 | 904             | 10            |
| 11| Hemicellulose + 5 O₂ → 4 H₂O + 5 CO₂         | 0.999                 | 904             | 10            |
| 12| Lignin + 10.125 O₂ → 6.95 H₂O + 7.3 CO₂     | 0.999                 | 904             | 10            |
| 13| Fructose + 6 O₂ → 6 H₂O + 6 CO₂              | 0.999                 | 904             | 10            |
| 14| Xylose + 5 O₂ → 5 H₂O + 5 CO₂                | 0.999                 | 904             | 10            |
| 15| Humins (from cellulose) + 6 O₂ → 5 H₂O + 6 CO₂| 0.999                 | 904             | 10            |
| 16| Humins (from hemicellulose) + 5 O₂ → 4 H₂O + 5 CO₂| 0.999                 | 904             | 10            |
| 17| H₂SO₄ + 2 NaOH → Na₂SO₄ + 2 H₂O             | 0.999                 | 70              | 6             |

AA: Acetic acid; HMF: 5-hydroximethylfurfural; LA: Levulinic acid; FA: Formica cid; EL: Ethyl levulinate.

Table 7
Distillation columns operation conditions.

| Distillation Column | Process Stage          | NS | FS | RR  | D:F | B:F | TSP (bar) | PD (bar) |
|---------------------|------------------------|----|----|-----|-----|-----|----------|---------|
| RF-110              | LA and FFR purification| 14 | 6  | 0.7 | N/A | 0.68| 0.2      | 0.25    |
| RF-201              | LA and FFR purification| 30 | 2  | 1.7 | 0.1 | N/A | 1.0      | 0.40    |
| RF-202              | LA and FFR purification| 12 | 6  | 0.5 | N/A | 0.8 | 1.0      | 0.30    |
| RF-301              | EL production          | 10 | 6  | 0.5 | N/A | 0.11| 1.0      | 0.30    |
| RF-302              | EL production          | 19 | 8  | 0.8 | 0.85| N/A | 0.2      | 0.25    |

NS: number of stages; FS: feed stage; RR: molar reflux ratio; D:F: distillate to feed ratio; B:F: bottoms to feed ratio; TSP: top stage pressure; PD: pressure drop of the column.
is presented in Table 11. The contribution analysis for the alternative scenario is presented in Fig. 13.

Finally, an economic assessment for the alternative scenario was performed. Table 12 shows the cost of raw materials, utilities, and the selling price of all products (i.e., FFR, LA, EL, sodium sulfate). Table 13 presents the cost distribution for all subroutines listed in Table 5. Table 14 and Table 15 portray the CAPEX and OPEX distribution.
3. Experimental Design, Materials and Methods

The purpose of this document is to gather all the relevant information to calculate the LCI to carry out the LCA to produce EL from RS, as shown in the main manuscript. Table 1 shows the methodology to calculate the LCI of each stage involved in the conversion of RS into EL. Detailed information is shown in the upcoming sections.
Fig. 11. Sensitivity analysis for RF-302. a) Number of stages; b) Feed stage; c) Molar reflux ratio; d) Distillate to feed ratio. LA = levulinic acid; EL = ethyl levulinate.

Table 8

| Stream                                    | Kind of stream | Unit   | Value  |
|-------------------------------------------|----------------|--------|--------|
| Rice straw (10 wt.% humidity)             | Input          | kg/h   | 2.000  |
| Ethanol (99 wt.%)                         | Input          | kg/h   | 108.9  |
| Sulfuric acid (80 wt.%)                   | Input          | kg/h   | 482.4  |
| Aqueous sodium hydroxide (50 wt.%)        | Input          | kg/h   | 623.3  |
| Water                                     | Input          | kg/h   | 1,601.2|
| Levulinic acid (98.7 wt.%)                | By-product     | kg/h   | 32.8   |
| Furfural (99.4 wt. %)                     | By-product     | kg/h   | 226.7  |
| Sodium sulfate (98.2 wt. %)               | By-product     | kg/h   | 563.1  |
| Ethyl Levulinate (99.5 wt. %)             | Main product   | kg/h   | 230.5  |
| Energy consumption                        | Energy input   | GJ/h   | 31.0   |
| Electricity                               | Energy input   | MJ/h   | 7.3    |
| Cooling water                             | Cooling input  | t/h    | 62.5   |
| Air                                       | Cooling input  | t/h    | 5,173.4|

4. Life Cycle Inventory

4.1. Rice straw production

LCI for the production of RS was obtained for Colombia conditions, in the Orinoquia region [2]. RS production encompasses both cultivation and harvest stages. An average paddy rice yield of 4.97 t/ha was used for inventory calculation [3]. Diesel, fertilizers, land resources, and energy were the main inputs. Emissions to air and water were also considered. Paddy rice and RS were considered as main outputs. Diesel, land, and fertilizer requirements for rice production was obtained from the literature review [2]. Emissions of the agricultural stage was determined according to the IPCC methodology. Emissions associated with the use of nitrogen fertilizers included NH₃, NOₓ, N₂O, and NO₃. The latter was calculated according to the SQCB (Sustainable Quick Check for Biofuels) methodology. Phosphorous emissions to water were calculated
using the SALCA (Swiss Agricultural Life Cycle Assessment) model [4]. Emissions associated with diesel combustion in the agroindustry were calculated based on the emissions factors reported by Martinez-Gonzales et al. [5]. CH₄ emission associated with rice cultivation was also included. Carbon sequestered by the crop was calculated in terms of the proximate analysis rice and the carbon content of each fraction as shown in Table 2 reported in literature [6]. Rainfall and irrigation needs were calculated using the TURC methodology. The LCI for paddy rice culture in Orinoquia region in Colombia is present in Table 3.
Fig. 12. Contribution analysis for base scenario for EL production from RS for a) acidification, b) climate change, c) freshwater eutrophication, d) marine eutrophication, e) ozone depletion, f) photochemical ozone formation, g) terrestrial eutrophication, and h) water resource depletion.

4.2. Rice straw valorization to EL

Fig. 1 shows a complete process to produce EL from RS was developed in Aspen Plus v.12 (Aspen Tech, MA, USA) by considering four main stages: (i) RS acid hydrolysis; (ii) purification of LA; (iii) purification of FFR; and (iv) production and purification of EL. The Non-Random Two-Liquid with Redlich-Kwon (NRTL-RK) was used as the main thermodynamic package for phase equilibrium and thermodynamic estimations. However, due to the scarcity of some binary parameters for modelling the equilibrium phase with 3,5-hydroxymethylfurfural (HMF) and other lignocellulosic by-products (e.g., FFR, LA, formic acid (FA) and acetic acid (AA)), the Dortmund modified UNIFAC (UNIFAC-DMD) group contribution was employed to calculate the activity coefficients. The UNIFAC-DMD provides more reliable behavior of the phase equilibria of compounds...
than the traditional UNIFAC method. RS was modelled in terms of cellulose (38.3 wt.%), hemicellulose (28 wt.%), lignin (14.9 wt.%), and ashes (18.8 wt.%) based on data presented in Table 2. The three former was modelled according to the properties shown by Wooley and Putsche [7]. Whereas ashes were modelled as dioxide silicon due to this is the main constitutive element in this biomass fraction. Humins were modelled as cellulose and hemicellulose since those are decomposition products during the acid hydrolysis of biomass. Auxiliary units such as heat exchangers, pumps, compressors, valves, mixers, and splitters were considered within the simulation of the overall process. Kinetics models for reactions were not considered due to the main objective with the simulation is to obtain mass and energy balances for life cycle inventory purposes and the sizing or design of the equipment is not part of the study scope.

Table 4 shows a description of main subroutines using in the process simulated with Aspen Plus v12. A brief description, as well as the operating conditions and assumptions used for each unit are presented. And Table 5 present the purpose of each subroutine employed among the simulation in Aspen Plus v12. Mixers and Flow Splitters were not considered for data presented in Table 4 and Table 5.

4.3. Rice straw pretreatment

Fig. 2 presents the detailed diluted acid hydrolysis flowsheet, which corresponds to the Hierarchy block name ACID-HYD shown in Fig. 1. Herein, steam explosion and diluted acid hydrolysis were employed together as pretreatment method to pretreat RS. Steam explosion was used as alternative to remove the hemicellulose fibers and ease the hydrolysis of hemicellulose and cellulose. In this first reaction stage, sulfuric acid was employed based on Biofine process at 210°C and 20 bar. A second diluted acid hydrolysis with sulfuric acid was employed since its widely used at industrial level to pretreat lignocellulosic biomass at 190°C and 18 bar. Table 6 shows the conversion rates of main reactions during the acid hydrolysis of RS and LA esterification based on the literature review. Aside from the acid hydrolysis stage, the pretreatment also includes the neutralization of sulfuric acid with sodium hydroxide, the recovery of unreacted cellulose, hemicellulose, lignin, and humins, hereafter names as HYD-SOL. Also includes the recovery of sodium sulfate as by-product for sale. All reactors employed to pretreat the biomass were RStoic subroutine. The heat generated in the first reaction stage was used to preheat the process water used for dilute acid hydrolysis. The liquid to solid ratio employed for dilute acid hydrolysis was 8:1, using a water recycle equivalent to 77% of the water used as solvent in the hydrolysis reaction. Two solid separation units were employed to separate the unreacted sugars and the sodium sulfate produced in the neutralization reactor (RS-103).

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**Table 10**

Mass and energy balance of the production of EL from rice straw in alternative scenario.

| Stream                                      | Kind of stream | Unit | Value  |
|---------------------------------------------|----------------|------|--------|
| Rice straw (10 wt.% humidity)               | Input          | kg/h | 2,000  |
| Ethanol (99 wt.%)                           | Input          | kg/h | 109.0  |
| Sulfuric acid (80 wt.%)                     | Input          | kg/h | 473.0  |
| Aqueous sodium hydroxide (50 wt.%)          | Input          | kg/h | 611.1  |
| Water                                       | Input          | kg/h | 1,862.2|
| Lower pressure steam (125°C)               | By-product     | kg/h | 3,100  |
| Medium pressure steam (175°C)              | By-product     | kg/h | 2,500  |
| Levulinic acid (98.7 wt.%)                 | By-product     | kg/h | 32.8   |
| Furfural (99.4 wt. %)                       | By-product     | kg/h | 226.7  |
| Sodium sulfate (98.2wt. %)                  | By-product     | kg/h | 552.2  |
| Ethyl Levulinate (99.5 wt. %)               | Main product   | kg/h | 230.7  |
| Energy consumption                          | Energy input   | GJ/h | 11.6   |
| Electricity                                 | Energy input   | MJ/h | 7.2    |
| Cooling water                               | Cooling input  | t/h  | 63.2   |
| Air                                         | Cooling input  | t/h  | 5,229.6|

| Process                        | Component                                      | Stream type | Unit     | Amount        |
|-------------------------------|-----------------------------------------------|-------------|----------|---------------|
| Hydrolysis                    | Air                                           | Input       | kg       | 4,987,483.000 |
| Hydrolysis                    | Heat, from steam, in chemical industry         | Input       | kWh      | 3,909.000     |
| Hydrolysis                    | Rice straw                                    | Input       | kg       | 2,000.000     |
| Hydrolysis                    | Sodium hydroxide, without water, in 50% solution state | Input      | kg       | 311.660       |
| Hydrolysis                    | Sulfuric acid                                 | Input       | kg       | 385.960       |
| Hydrolysis                    | Transport, freight, lorry 3.5-7.5 metric ton, EURO3 | Input     | kg/km    | 60,000.000    |
| Hydrolysis                    | Water, unspecified natural origin, CO         | Input       | m³       | 2.220         |
| Hydrolysis                    | Liquid hydrolyzed                             | Output      | kg       | 8,790.988     |
| Hydrolysis                    | Sodium sulfate, anhydrite                      | Output      | kg       | 563.090       |
| Hydrolysis                    | Solid hydrolyzed                              | Output      | kg       | 1,107.000     |
| Production of LA             | Air                                           | Input       | kg       | 219,527.000   |
| Production of LA             | Heat, from steam, in chemical industry         | Input       | kWh      | 242.000       |
| Production of LA             | Liquid hydrolyzed                             | Input       | kg       | 8,790.988     |
| Production of LA             | Low Pressure Steam                            | Input       | kg       | 1,537.000     |
| Production of LA             | Medium Pressure Steam                         | Input       | kg       | 2,500.000     |
| Production of LA             | Water, cooling, unspecified natural origin, CO| Input       | m³       | 263.728       |
| Production of LA             | Acetic acid                                   | Emission to water | kg | 4,180        |
| Production of LA             | Formic acid                                   | Emission to water | kg | 89.570      |
| Production of LA             | Furfural                                      | Emission to water | kg | 11.760      |
| Production of LA             | Furfural, 98.5 wt.%                           | Output      | kg       | 227.000       |
| Production of LA             | Glucose                                       | Unmapped flow/water, unspecified | kg | 102.630    |
| Production of LA             | Levulinic acid                                | Output      | kg       | 221,103       |
| Production of LA             | Wastewater/m3                                 | Emission to water | m³ | 2.342       |
| Production of EL             | Air                                           | Input       | kg       | 22,611.000    |
| Production of EL             | Electricity, medium voltage                   | Input       | kWh      | 0.259         |
| Production of EL             | Ethanol, without water, in 99.7% solution state, from fermentation | Input | kg | 108.951 |
| Production of EL             | Heat, from steam, in chemical industry         | Input       | kWh      | 316.211       |
| Production of EL             | Levulinic acid                                | Input       | kg       | 221,103       |
| Production of EL             | Water, cooling, unspecified natural origin, CO| Input       | m³       | 53.122        |
| Production of EL             | Zeolite, powder                               | Input       | kg       | 0.001         |
| Production of EL             | Ethanol                                       | Emission to water | kg | 33.590      |
| Production of EL             | Ethyl levulinate                              | Output      | kg       | 230.489       |
| Production of EL             | Furfural                                      | Emission to water | kg | 0.100       |
| Production of EL             | Levulinic acid                                | Output      | kg       | 32.810        |
| Production of EL             | Water, CO                                     | Emission to water | m³ | 0.030       |
| Solid Combustion             | Air                                           | Input       | kg       | 13,000.000    |
| Solid Combustion             | Solid hydrolyzed                              | Input       | kg       | 1,107.000     |
| Solid Combustion             | Water, turbine use, unspecified natural origin, CO | Input | m³ | 0.281       |
| Solid Combustion             | Carbon dioxide, biogenic                       | Emission to air | kg | 1,663.460    |
| Solid Combustion             | Electricity                                   | Output (Avoided product) | kWh | 116.000     |
| Solid Combustion             | Low Pressure Steam                            | Output      | kg       | 3,100.000     |
| Solid Combustion             | Medium Pressure Steam                         | Output      | kg       | 2,500.000     |
| Solid Combustion             | Nitrogen                                      | Emission to air | kg | 9,971.000    |
| Solid Combustion             | Water, CO                                     | Emission to water | m³ | 0.581       |
| Solid Combustion             | Wood ashes                                    | Waste/unspecified | kg | 338.030     |

LA = levulinic acid; EL = ethyl levulinate.
4.4. Levulinic acid and furfural purification

Fig. 3 (LA production) present the detailed flowsheet for LA purification. Distillation column was modelled using a RadFrac module with Strongly non-ideal liquid convergence method. The purification of LA was designed based on the literature review, where a distillation train formed by two flash separators and a distillation column was used. Flash separators were modelled using Flash-2 module, and the heat remnant from the vapor phase of the first flash unit was used to reheat the liquid phase feed to the second flash unit. The flash units were modeled as adiabatic units and no pressure drop inside de vessel. Temperature and pressure conditions required for each flash were set using a heat exchanger and a valve before each flash feed.
Table 12
Cost of purchase of raw materials and utilities and selling price for by-products.

| Component               | Type      | Value | Unit    | Reference |
|-------------------------|-----------|-------|---------|-----------|
| Rice straw              | Input     | 0.025 | USD/kg  | [9]       |
| Ethanol                 | Input     | 0.9355| USD/kg  | [9]       |
| Sulfuric acid           | Input     | 0.0991| USD/kg  | [9]       |
| Sodium hydroxide        | Input     | 0.01275| USD/kg  | [10]      |
| Water process           | Utility   | 0.00108| USD/kg  | [11]      |
| Cooling water           | Utility   | 0.001318| USD/kg  | [11]      |
| Electricity             | Utility   | 0.193 | USD/kWh | [12]      |
| Medium pressure steam   | Utility   | 0.008627| USD/kg  | [9]       |
| High pressure steam     | Utility   | 0.01039| USD/kg  | [9]       |
| Propane (Refrigerant)   | Utility   | 0.674 | USD/kg  | [9]       |
| Air                     | Utility   | -     | -       | -         |
| Furfural                | By-product| 2.2   | USD/kg  | [13]      |
| Levulinic acid          | By-product| 5.0   | USD/kg  | [14]      |
| Sodium sulfate          | By-product| 0.095 | USD/kg  | [15]      |
| Ethyl levulinate        | Main product| 3.0   | USD/kg  | [16]      |

Fig. 4 (FFR purification) presents the detailed flowsheet for FFR purification. The FFR purification was carried out using azeotropic distillation based on Zeitsch [8]. Azeotropic distillation columns were also modelled with RadFrac module but using the Azeotropic convergence method. Efficiency of distillation columns were adjusted to 65% according to heuristics rules. A decanter was used to separate the distillate from the first distillation tower into a furfural-rich phase, which was subsequently distilled to obtain a high purity FFR stream and the removal of volatiles such as formic acid (FA) and the remaining water in the distillate. The aqueous rich phase from decanter DC-201 was recirculated to the azeotropic column to maximize FFR recovery. The bottom stream from RF-201 (azeotropic column) was recycled to the dilute acid hydrolysis stage to reduce the total water consumption of the overall process and to minimize the FFR lost in the two-step separation train.

4.5. Ethyl levulinate production

Fig. 5 presents the detailed flowsheet for EL production. This was done through the esterification of LA with ethanol using a desilicated DH-ZSM-5 zeolite as catalyst with a catalyst load of 13wt%. Esterification was modelled with a RStoic unit at 120°C and 4.5 bar, using ethanol as solvent (8:1 ratio) with a conversion of LA of 85% as shown in Table 6. Kinetic model for this reaction was not considered due to the simulation purpose is not the equipment design or sizing instead the mass and energy balances calculation for LCI. Purification of EL was performed by using a distillation train where RadFrac modules with Strongly non-ideal liquid convergence method were employed to module the two distillation columns. Efficiency of distillation columns were adjusted to 65% according to heuristics rules. In the first column, a distillate rich in ethanol and water is obtained, which is subjected to a separation process with molecular sieves for the recovery and recirculation of 95% of the remaining ethanol using a SEP-2 unit. The bottom stream, containing LA and EL is fed to a second distillation tower, where two high purity streams are obtained, one of EL and the other of LA.

4.6. Heat integration

The integration consisted of using the remaining heat from the first acid hydrolysis reactor and the output stream of the second acid hydrolysis reactor to reduce the energy consumption associated with the generation of the steam required for hydrolysis, according to Fig. 2. Likewise, the two steam streams obtained from the flash units associated with the separation of the FFR
Table 13
Cost distribution for all subroutines in the Aspen Plus process simulation.

| Hierarchy Block | Subroutine Name | Equipment Cost [USD] | Installed Cost [USD] |
|-----------------|-----------------|----------------------|---------------------|
| ESTERIF         | HT-302-H        | $9,200               | $52,800             |
| ESTERIF         | P-302           | $4,700               | $31,000             |
| ESTERIF         | P-301           | $4,600               | $30,800             |
| ESTERIF         | RS-301          | $48,600              | $191,100            |
| ESTERIF         | B4              | $17,100              | $107,400            |
| ESTERIF         | RF-301-cond     | $11,100              | $67,300             |
| ESTERIF         | RF-301-cond acc | $17,300              | $116,500            |
| ESTERIF         | RF-301-reb      | $18,700              | $78,100             |
| ESTERIF         | RF-301-reflux pump | $5,000           | $30,200             |
| ESTERIF         | RF-301-tower    | $49,200              | $219,500            |
| ESTERIF         | HT-301-H        | $9,500               | $66,700             |
| ACID-HYD        | RS-102          | $88,600              | $246,900            |
| ACID-HYD        | HT-103-C        | $17,000              | $86,200             |
| ACID-HYD        | H101            | $27,200              | $118,200            |
| ACID-HYD        | SS-102          | $390,000             | $579,800            |
| ACID-HYD        | HT-101-H        | $21,400              | $125,300            |
| ACID-HYD        | P-101           | $16,900              | $44,700             |
| ACID-HYD        | RS-103          | $84,600              | $239,500            |
| ACID-HYD        | SS-101          | $390,000             | $579,800            |
| ACID-HYD        | RS-101          | $88,600              | $249,200            |
| ACID-HYD        | HT-103-C        | $150,600             | $296,300            |
| ACID-HYD        | HT-102-H        | $21,100              | $107,900            |
| FFR-SEP         | HT-204-C        | $17,100              | $116,600            |
| FFR-SEP         | HT-202-C        | $9,200               | $50,000             |
| FFR-SEP         | RF-201-cond     | $15,600              | $82,500             |
| FFR-SEP         | RF-201-cond acc | $17,300              | $117,700            |
| FFR-SEP         | RF-201-reb      | $35,600              | $118,500            |
| FFR-SEP         | RF-201-reflux pump | $5,000           | $31,400             |
| FFR-SEP         | RF-201-tower    | $119,700             | $312,800            |
| FFR-SEP         | P-201           | $4,400               | $30,700             |
| FFR-SEP         | HT-201-C        | $24,000              | $102,800            |
| FFR-SEP         | P-303           | $17,900              | $52,300             |
| FFR-SEP         | M201            | $12,100              | $72,500             |
| HYD-SEP         | RF-110-cond     | $8,700               | $48,400             |
| HYD-SEP         | RF-110-cond acc | $17,300              | $110,500            |
| HYD-SEP         | RF-110-reb      | $14,000              | $64,800             |
| HYD-SEP         | RF-110-reflux pump | $5,000           | $30,200             |
| HYD-SEP         | RF-110-tower    | $35,400              | $192,600            |
| HYD-SEP         | FL-111-flash vessel | $17,100         | $115,100            |
| HYD-SEP         | HT-111-C        | $16,100              | $83,000             |
| HYD-SEP         | SEP-110         | $17,100              | $115,100            |
| HYD-SEP         | HT-110-H        | $18,000              | $103,600            |
| HYD-SEP         | FL-110-flash vessel | $19,800         | $119,000            |
| HYD-SEP         | HT-112-H        | $18,100              | $103,500            |
| HEAT-GEN        | HT-401-H        | $20,500              | $104,700            |
| HEAT-GEN        | TUR-401         | $115,700             | $285,600            |
| HEAT-GEN        | HT-403-C        | $15,700              | $82,600             |
| HEAT-GEN        | P-402           | $5,300               | $35,600             |
| HEAT-GEN        | HT-402-C        | $12,100              | $69,700             |
| HEAT-GEN        | HT-404-C        | $21,000              | $100,000            |
| HEAT-GEN        | TUR-402         | $116,400             | $275,900            |

and the LA were integrated for heating the liquid hydrolysate entering the separation train of the HYD-SEP hierarchy, according to Fig. 3 (HYD-SEP) and Fig. 4 (FFR-SEP). The other streams were not integrated because their flows were too small, and the temperature differences did not satisfy the minimum temperature approach value of 10°C. The MHeatX unit was employed to model de heat exchangers associated with the heat integration implementation.
Table 14
CAPEX distribution by items using Lang Factors for alternative scenario.

| CAPEX                        | Solid-fluid processing plant | Value (USD) |
|------------------------------|------------------------------|-------------|
| Direct costs                 |                              |             |
| Purchased equipment          | 1                            | $2,262,200  |
| Delivery, percent of purchased equipment | 0.1                          | $226,220    |
| Purchased equipment installation | 0.39                        | $882,258    |
| Instrumentation and controls | 0.26                         | $588,172    |
| Piping                       | 0.31                         | $701,282    |
| Electrical                   | 0.1                          | $226,220    |
| Buildings                    | 0.29                         | $650,038    |
| Yard improvement             | 0.12                         | $271,464    |
| Service facilities           | 0.55                         | $1,244,210  |
| Total direct costs           |                              | $7,058,064  |
| Indirect costs               |                              |             |
| Engineering and supervision  | 0.32                         | $723,904    |
| Construction expenses        | 0.34                         | $769,148    |
| Legal expenses               | 0.04                         | $90,488     |
| Contractor’s fees            | 0.19                         | $429,818    |
| Contingency                  | 0.37                         | $837,014    |
| Working capital              | 0.75                         | $1,696,650  |
| Total indirect costs         |                              | $4,547,022  |
| CAPEX                        |                              | $11,605,086 |

4.7. Combustion of solid hydrolyzed residue

Fig. 6 presents the detailed flowsheet for LPS and MPS generation. RStoic unit was used to model combustion by stoichiometric reactions of solid waste combustion assuming complete combustion and disregarding the generation of methane, NOx, and SOx. The combustion temperature was set in 904°C at a pressure of 10 bar. Excess air was used to control the reactor temperature.

The condenser was modeled using a Heater unit cooled by air and the boiler was modeled using a non-rigorous MHeatX unit. Ashes from the combustion unit was separated from the reactor outlet stream using an SEP-2 unit. Two isentropic turbines were used to generate the MPS (saturated steam at 175°C) and the LPS (125°C). A total of 5,600 kg/h of water was used to generate 3,100 kg/h of LPS (100% of the requirement of the process) and 2,500 kg/h of MPS (55% of the total process requirement). Both LPS and MPS generated was recirculated to the generation cycle, reducing the water consumption to a make-up stream of 280 kg/h of water.

4.8. Sensitivity analysis for distillation columns design

A sensitivity analysis was performed to determine the best operation conditions for the five distillation columns used among the process. The number of equilibrium stages, optimal feed stage, reflux molar ratio, and distillation or bottom to feed ratio were assessed to minimize the energy requirements in the distillation column and maximize the recovery of the interest product.

Table 7 presents the operation conditions selected for each distillation column. Detailed sensitivity analysis is shown in Fig. 7 (RF-110), Fig. 8 (RF-201), Fig. 9 (RF-202), Fig. 10 (RF-301), and Fig. 11 (RF-302). The operation pressures were selected seeking the reduction of reboiler and condenser duty requirement.
Table 15
OPEX distribution by item using Lang Factors for alternative scenario.

| Variable production costs                   | Value (USD)  |
|---------------------------------------------|--------------|
| Raw materials                               | $1,542,598   |
| Operating labor                             | $885,177     |
| Direct supervisory and clerical labor       | $88,518      |
| Utilities                                   | $1,770,354   |
| Maintenance and repairs                     | $580,254     |
| Operating supplies                          | $116,051     |
| Laboratory charges                          | $88,518      |
| Patents and royalties                       | $354,071     |
| Total variable production costs             | $5,425,540   |
| Fixed charges                               |              |
| Local taxes                                 | $464,203     |
| Insurance                                   | $116,051     |
| Rent                                        | $696,305     |
| Financing (interest)                        | $290,127     |
| Total fixed charges                         | $1,566,687   |
| Plant overhead costs                        | $1,062,212   |
| General expenses                            |              |
| Administrative costs                        | $265,553     |
| Distribution and marketing costs            | $885,177     |
| Research and development costs              | $442,589     |
| Total general expenses                      | $1,593,319   |
| OPEX (USD/year)                             | $9,647,758   |

4.9. Mass and energy balance, Life Cycle Inventory, and Contribution Analysis

Mass and energy balance were retrieved from the simulation results in Aspen Plus. The Life Cycle Inventory (LCI) was estimated using the Aspen Plus balances and the Ecoinvent Database for background data. Contribution analysis was performed in Open LCA v.1.10 software using the ILCD 2011 midpoint + baseline method with eight impact categories assessed: (1) Acidification (molc H+ -eq); (2) Climate Change (kg CO2-eq); (3) Freshwater Eutrophication (kg P-eq); (4) Marine Eutrophication (kg N-eq); (5) Ozone Depletion (kg CFC-11-eq); (6) Photochemical Ozone Formation (kg NMVOC-eq); (7) Terrestrial Eutrophication (molc N-eq); and (8) Water Resource Depletion (m3 water-eq).

4.10. Base scenario

Table 8 presents the mass and energy balance to produce EL from RS in the base scenario. Fig. 12 presents the contribution analysis of all impact categories described above in the base scenario. Finally, Table 9 presents the LCI of the production of EL from RS in the base scenario.

4.11. Alternative scenario

Table 10 presents the mass and energy balance to produce EL from RS in the alternative scenario and Table 11 presents the LCI of the production of EL from RS in the alternative scenario. Finally, Fig. 13 shows the LCI of the production of EL from RS using a paddy rice yield of 5.7 t/ha.
4.12. Economic assessment

An economic assessment for the alternative scenario was performed to give insights into the feasibility of the process in an integrated way. Table 12 presents the cost of raw materials, products, by-products, and co-products retrieved from the literature review and used for calculation of economic indicators.

Table 13 presents the equipment cost and installation cost, obtained from Aspen Plus Economic Analyzer and used for CAPEX calculation. Table 14 depicts the CAPEX distribution estimated using Lang-Factors and Table 15 present the OPEX distribution using Lang-Factors.

Ethics Statement

This work did not involve human subjects or laboratory animal, therefore did not meet any ethical issues.

CRediT Author Statement

Cristhian Cañon: Writing – original draft preparation, Visualization, Investigation, Process Simulation; Nestor Sanchez: Conceptualization, Methodology, Writing – review & editing; Martha Cobo: Conceptualization, Methodology, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

Data Availability

Ethyl_Levulinate_from_Colombian_Rice_Straw (Original data) (Mendeley Data)
Life Cycle Inventory data for ethyl levulinate production from Colombian rice straw (Original data) (Data in brief).

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