Production of Hemicellulosic Sugars from Residual Lignocellulosic Biomass in an Integrated Small-Scale Biorefinery: Techno-Economic and Life Cycle Assessments

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Abstract

Biorefineries design, as for other industries, usually target the economy of scale approach, maximizing processing capacities to achieve economic viability. However, the installation of large-scale biorefineries has some drawbacks, namely their high capital costs and the difficulty to assure a proper supply of biomass at regional level. Small-scale, self-sustainable, biorefineries can solve several of the challenges of their larger competitors and are also reported to expand environmental and social benefits, but several hurdles for their deployment still exist.

This chapter describes a methodology for the implementation of an integrated small-scale self-sustainable biorefinery in a rural area, based on a design that takes advantage of the synergies of processing two types of feedstock (corn stover and swine manure). A detailed explanation for the process selection by performing a heuristic analysis, process simulation, mass and energy balances alongside with the techno-economic assessment of the biorefinery is provided. The full life cycle assessment (LCA) of producing xylo-oligosaccharides (XOS) and ethanol from lignocellulosic residues, i.e. corn stover, under a biorefinery concept to be located in Portugal is also assessed.

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Keywords

Lignocellulosic residues · Hemicellulosic sugars · Biorefinery · Life cycle assessment · Xylo-oligosaccharides · Ethanol

3.1 Introduction

Biorefineries have initially followed the concept of traditional, crude oil based, refineries, targeting the use of only a single feedstock within plants presenting large processing capacities in order to achieve economic sustainability through an economy of scale approach. Under this framework, most rural areas in Europe and even worldwide fail to sustain effective conditions to install such biorefineries. Several studies point out that high CAPEX and OPEX are the main bottlenecks, together with the inability of most regions to support per se a sustainable large supply of biomass (Chandel et al. 2018). An alternative approach relies on the onset of small-scale biorefineries in rural areas. These would be able to overcome most of these challenges, strengthening territorial economic cohesion and generating local direct and indirect jobs (de Visser and van Ree 2016). Small-scale enables a substantial cost reduction related to feedstock transportation, as well as of intermediate products leading to a direct link between the primary sector and industry, supporting the bioeconomy onset and progress. In spite of the recognized strategic importance of small-scale biorefineries, there are still various technological, operational, and policy challenges hampering their commercial deployment (Balan 2014). For instance, in temperate and tropical regions, there is a great diversity of bio-resources (ranging from crop and forestry residues to animal waste, and industrial agro-food processing residues) that lack proper logistic and political support, as well as technological solutions to enable their concomitant valorization.

A possible technological strategy to tackle this diversity/heterogeneity is the combination of two or more of the diverse biorefinery platforms: the use of (a) typical biochemical platform processes to transform lignocellulosic feedstock into sugars and lignin-rich streams that can be concomitantly converted into biofuels (e.g. bioethanol or higher alcohols), and/or added-value chemicals, and (b) the anaerobic digestion platform converting wet biomass and side streams into biogas (Bharathiraja et al. 2016). The later can be upgraded into biomethane and sold or used for plant own consumption. This example of a small-scale integrated biorefinery is able to take advantage of both dry and wet bio-resources to produce a significant portfolio of diverse bioproducts, thus maximizing feedstock utilization, energy efficiency, and overall sustainability of the whole value chain.

Under this framework, the lignocellulosic biomass pre-treatment is an important and often restrictive step for the efficient processing of biomass in a biorefinery, being the hydrothermal processes (e.g., autohydrolysis) a clean and efficient pathway for the production of two upgradable streams: the liquid stream, hemicellulose-rich, and on the other hand, the solid cellulose-rich stream (Gírio et al. 2010). Oligosaccharides, particularly xylo-oligosaccharides (XOS), as emerging food additives presenting many functional properties (most noteworthy, the prebiotic effect), can be targeted as the high added-value product from the hemicellulose-rich liquor (Samanta et al. 2015; Moniz et al. 2016; Gullón et al. 2017; Turck et al. 2018). Bioethanol can be targeted as the main bulk products to be derived from the cellulose-rich solid fraction.

This chapter proposes and assesses the advantages of such small-scale, integrated biorefinery. It follows a heuristic analysis for best scenario selection, and the subsequent detailed process modelling and simulation using computer-aided process engineering tools to ascertain process feasibility at industrial scale (Moncada et al. 2013; Mussatto et al. 2013; Quintero et al. 2013). The influence of external factors in the economic sustainability of such a small-scale biorefinery, the identification of the major factors impacting its environmental sustainability, and the legal framework for its implementation are also assessed.

3.2 Heuristic Analysis

When assessing the economic and environmental viability of a biorefinery, it is important to evaluate the possible scenarios on a preliminary basis. Thus, a heuristic approach related with the design of a biorefinery system using the available feedstock, preliminary mass balances, process scale, matureness level of technologies, and product competitors must be performed beforehand (Cardona Alzate et al. 2004, 2019).

The following procedure is recommended to be applied in case studies with the purpose of justifying and better understanding the small-scale biorefineries potential, before proceeding to detailed Process Modelling and Simulation.

3.2.1 Feedstock

(a) Availability—The feedstock's availability (type of residues, available amount per year, etc.) for each selected region shall be evaluated.
(b) Accessibility—The accessibility to the selected feedstock in terms of logistics, annual production, competing uses, shall be assessed.

3.2.2 Biorefinery Design

Based on the chosen feedstock and expertise in biomass/bioproducts transformation, a preliminary knowledge-based conceptual design was applied. For this, a preliminary process flowsheet for the biorefinery case-study was built, as it is shown in the example of Fig. 3.1.

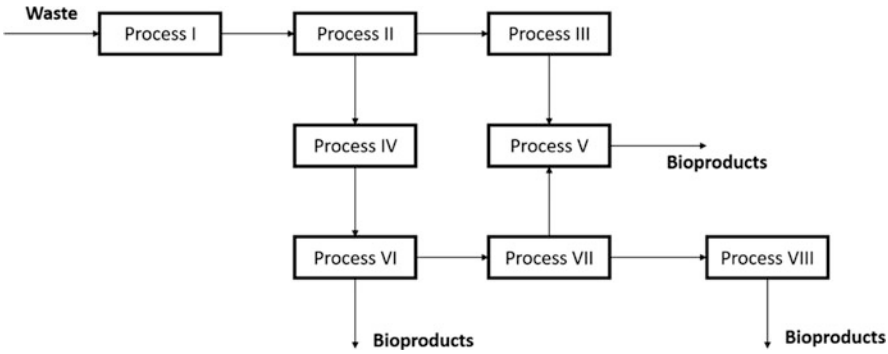

Fig. 3.1 Example of a typical biorefinery flowsheet

3.2.3 Preliminary Assessments

After building a first scenario for the biorefinery design, a preliminary mass and energy balance with the available feedstock for each region shall be performed.

These preliminary balances will help to select the process scale, based on the total amount of final product that can be produced using the available feedstock and the biorefinery design scenario.

Furthermore, a preliminary economic assessment shall be performed to predict scenarios viability under the selected conditions. For that, the most representative operating costs (OPEX) must be calculated as well as the main equipment capital costs (CAPEX). The economic viability can be assessed by calculating the net present value (NPV[1]) for a selected scale, being economically viable when NPV > 0.

3.2.4 Process Scale Selection

Afterwards, the biorefinery scale (that shall be small-scale[2]) should defined using one of the following options (Serna-Loaiza et al. 2019):

A. Define a range (minimum and maximum) based on the availability and accessibility of feedstock.

[1] NPV—Net Present Value: $\text{NPV} = \sum_{n=0}^{n=\text{project lifetime}} \frac{\text{Cash Flow}}{(1+\text{interest})^n}$ (Sadhukhan et al. 2014)

[2] Small-scale was defined by comparison of the amount of final product obtained with the produced amount in industrial scale of the same products, that for the present analysis should differ at least in one order of magnitude. For the cases where more than one product is obtained, the same approach is applied to the biomass processed.

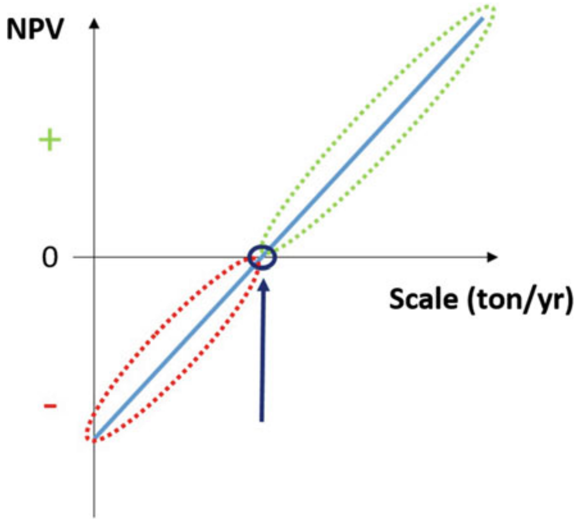

Fig. 3.2 Example of net present value variation with process scale

B. Find the minimum process scale to have NPV (net present value) > 0 and evaluate what can be improved in the process for scales where NPV < 0 (Fig. 3.2).
C. Fix the scale (at a small-scale basis).

All this analysis can be performed without any in-depth calculations and just using literature, previous experience, and basic preliminary calculations.

3.2.5 Process Technologies Choice

After selecting the scale, the biorefinery design must be improved, and the unit operations choice properly justified. For the Biorefinery Process Design in a case study, the choice of the unit operations should be based on these aspects: (a) final product quality (market requirement) and (b) technology matureness at industrial scale.

The matureness of technologies on industrial plants (small-scale) can be categorized in three different levels:

- Level 1—Type of technology with relatively low exploitation in the industry; R&D work.
- Level 2—Technology already exploited in the industry but not fully optimized.
- Level 3—Mature technology at industrial scale, fully established.

For each possible scenario, the matureness level of each technology shall be listed to help with a final decision on the most appropriate pathway to follow. As an example, Table 3.1 presents an assessment of a hypothetical scenario within an

Table 3.1 Example of the matureness level assessment of the technologies

Unit operation	Pressing	Reverse osmosis	Ultra-filtration	Electrodialysis	Ion exchanger	. . .
Matureness level	3	2	2	1	2	. . .

assessment. The chosen technologies for the whole process should be listed and categorized on their matureness at industrial scale.

Technologies with matureness level "1" must be *totally avoided* when designing a small-scale biorefinery. Only for specific cases, when no other options are available or, for instance, if it is the only known type of technology to obtain the required product purity, etc. Technologies with matureness level "2" should only be used if properly justified (based on energy consumption, product properties, process restrictions, subsequent units' requirements, etc.). Technologies with matureness level "3" have no restrictions.

3.2.6 Evaluation of Product Competitors

Product selection and biorefinery design shall be evaluated also based on the final product competitors in the region under assessment:

(a) One shall assess the market needs and specificities for the possible products for the feedstock in the region or in the surrounding regions, and evaluate the existing competitors.
(b) Different scenarios should be assessed based on different possible products, added-value products, energy/heat production, etc. The scenario choice must be justified based on the revenues, the competitors' sale price, the logistics (product transport and distribution to the buyers).

Figure 3.3 shows an example of different scenarios based on the possible products that can be obtained and a comparison based on the achieved profit.

3.2.7 Process Modelling

Once all steps described from 2.1 to 2.6 are complete, and the process design is properly justified and established, it will be able to proceed to detailed Process Modelling and Simulation using a commercial software like Aspen Plus (Aspen Technology, Inc.), SuperPro Designer (Intelligen, Inc.), or similar.

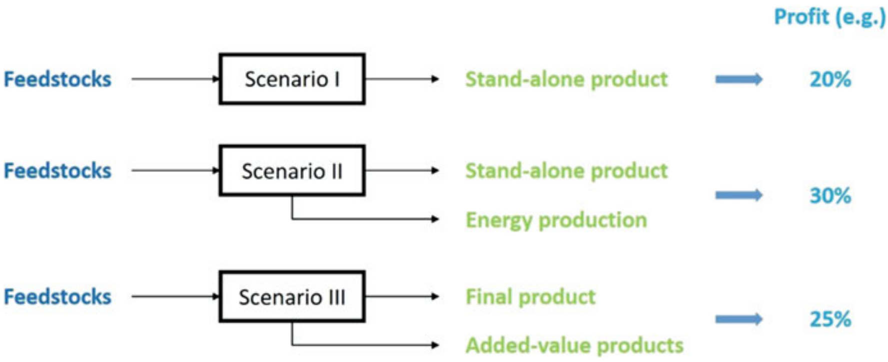

Fig. 3.3 Example of different scenarios based on different biorefinery products

Table 3.2 Feedstock characterization

Component	Value	Units
Glucan	40.83	%
Xylan	23.48	%
Arabinan	3.06	%
Lignin	16.91	%
Others	15.72	%

3.2.8 Application of the Heuristic Approach to the Case-Study

This case-study consists in an integrated small-scale biorefinery to be developed in Portugal. This assessment has considered the available residual lignocellulosic biomass and high-carbon content biomass for anaerobic digestion in the continental territory, and the possible synergies within the rural areas.

3.2.8.1 Available Feedstock

Portugal has very advantageous conditions for corn cultivation, presenting productivities that can exceed 14 ton/ha (*ANPROMIS* 2020), ranking among the highest worldwide. The main agricultural residues from this crop are the cobs and stalks, including leaves, typically called corn stover, which can account between 70 and 90%, by weight, of the produced corn grain, depending on the agricultural productivity, with higher grain productivities presenting a lower residue to grain ratio. Currently, these residues are mainly left in the field, taking not only a long time to be degraded, but also having significant impact on greenhouse gas production. In Portugal, about 110,000 ha of the best available soils are used for corn cultivation (Instituto Nacional de Estatística, 2018). Therefore, corn residues (namely corn stover) have great potential for being used in a biorefinery concept.

For the base-case scenario and in a 50 km radius around Chamusca region (ca. 25 km north from Lisbon, Portugal), ca. 100,000 ton/year of dry corn stover (Table 3.2) are available (200,000 ton/year if 100 km radius is considered). Regarding the accessibility to the feedstock (logistics, annual production, competitors, etc.), around 30% of the total amount at least is considered to be accessible to be used within the biorefinery. Therefore, 30,000 ton/year of corn stover is the minimum available dry biomass feedstock. Furthermore, in this region there are also many livestock farms producing important amounts of swine manure.

3.2.8.2 Biorefinery Design

The dominating strategy for fuel ethanol production from biomass (Gírio et al. 2010) relies on the initial removal of hemicellulose from the lignocellulosic materials. This fraction is extremely relevant to the economic feasibility of a lignocellulosic biomass-based biorefinery, not only by the co-fermentation of hemicellulose together with cellulose sugars can lead to higher amounts of bioethanol, but mainly through the production of oligosaccharides and/or monomeric sugars.

Thus, having that into account and based on the chosen feedstock, the following four scenarios were assessed:

- **Scenario A** (Fig. 3.4): solid and liquid fractions are separated. Liquid fraction (hemicellulose) is concentrated by evaporation in order to produce **pentose molasses**. Solid fraction (cellulose-rich, cellulolignin) is subject to enzymatic hydrolysis and fermented to produce **ethanol** via separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF);

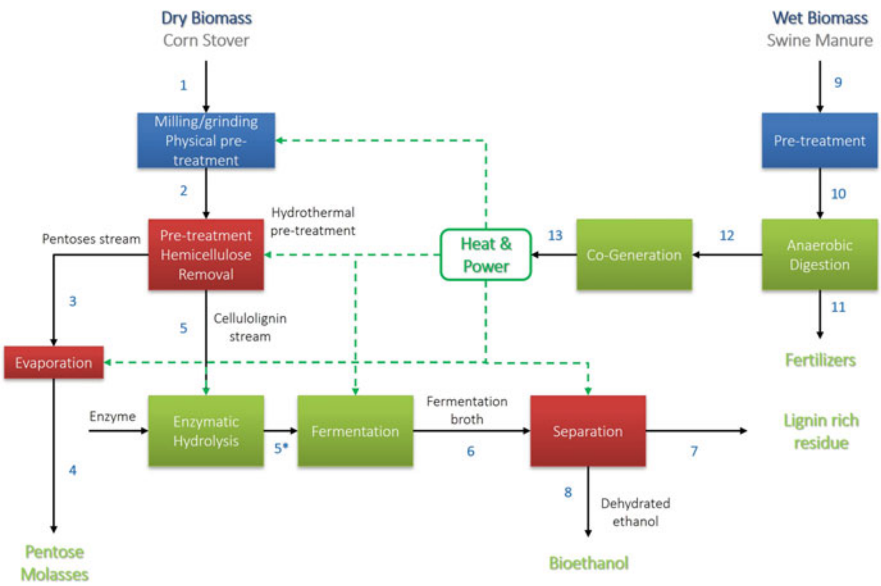

Fig. 3.4 Simplified block flow diagram of the processes involved in Scenario A

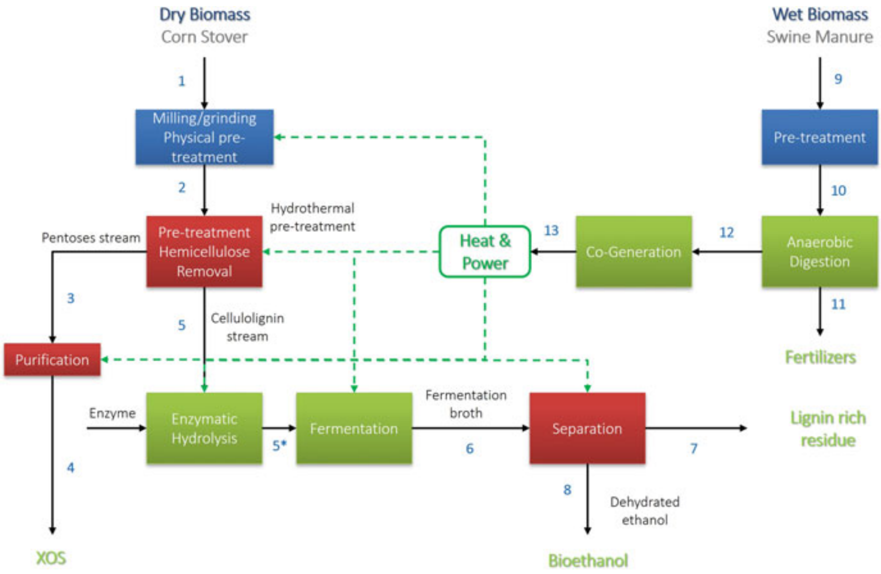

Fig. 3.5 Simplified block flow diagram of the processes involved in Scenario A′

- **Scenario A′** (Fig. 3.5): liquid fraction (hemicellulose) undergoes a purification step using membranes, in order to obtain **xylo-oligosaccharides** (XOS), besides producing **ethanol** from solid fraction (cellulolignin);
- **Scenario B** (Fig. 3.6): the slurry obtained after pre-treatment follows a pre-liquefaction with enzymes and is then fermented in a SSCF mode (simultaneous saccharification and co-fermentation of pentoses and hexoses) to produce **ethanol**;
- **Scenario C** (Fig. 3.7): liquid fraction (hemicellulose) is conveyed to acid post-hydrolysis step in order to obtain monomeric sugars (mainly pentoses) that will be converted to **xylitol** by a yeast strain. The solid fraction is processed as in scenario A to produce **ethanol**.

As mentioned before, associated to these agriculture crops, there are also livestock farms producing important amounts of swine manure that must be treated for environmental reasons and which can also be used for energetic valorisation using anaerobic digestion.

The process consists in the degradation of the organic matter, contained in the piggery effluents, and its conversion into a digested flow and a gaseous flow energy carrier (**biogas**). Through this process, the effluents are valorised and the negative environmental impacts associated to pig farming practice are avoided. The products of the anaerobic digestion—digested stream for irrigation and soil fertilization and

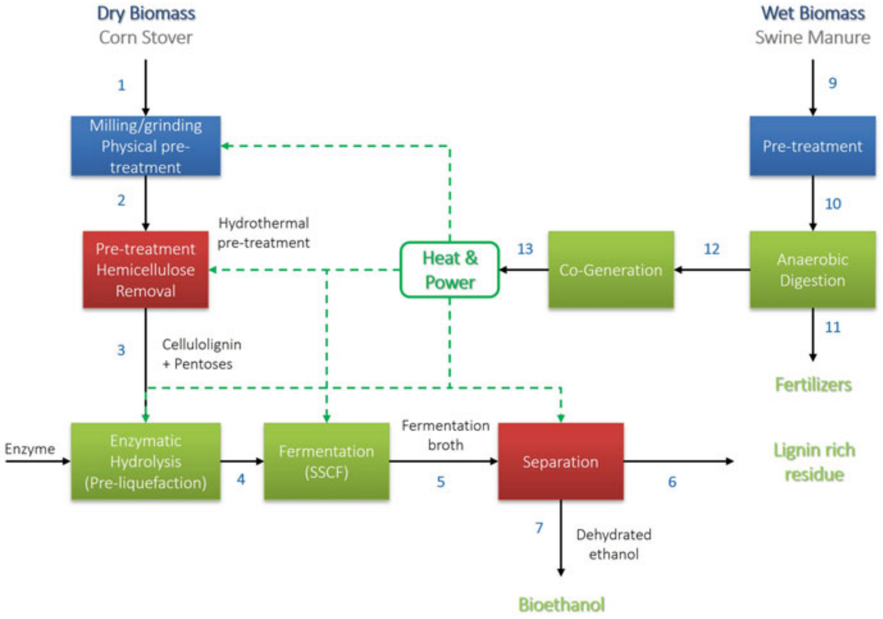

Fig. 3.6 Simplified block flow diagram of the processes involved in Scenario B

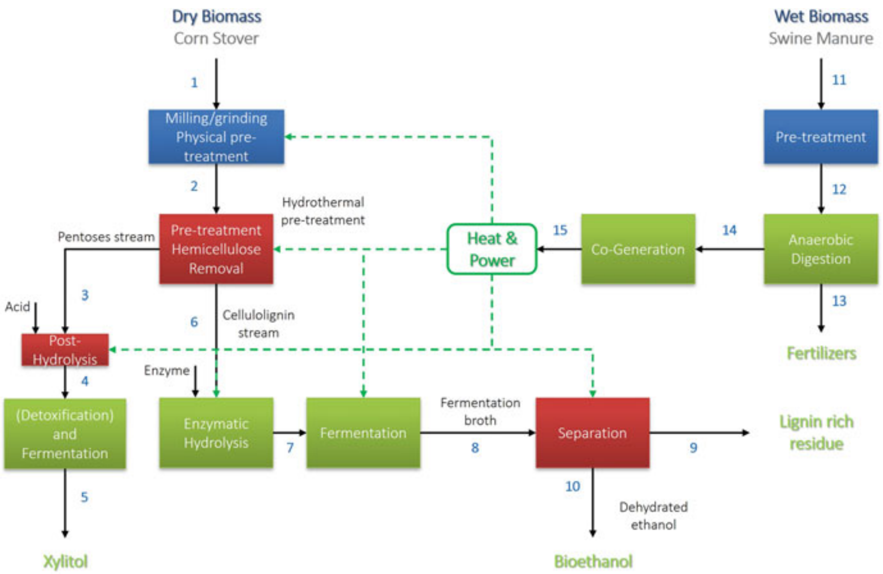

Fig. 3.7 Simplified block flow diagram of the processes involved in Scenario C

energy carrier gas, useful to **heat/power/fuel gas**—are applied to contribute in the best way to the sustainability of the whole process.

3.2.8.3 Technology Matureness Level

Regarding the industrial matureness level of the assessed scenarios, the leading technologies were evaluated. For Scenario A (Table 3.3) all technologies are well established at an industrial level. In Scenario A′ (Table 3.4), XOS purification is still under pilot-scale development; thus, the level 2 was attributed for the separation step. In Scenario B (Table 3.5), the co-fermentation of C5/C6 sugars is not yet completely established at an industrial scale, so that a level 2 was also attributed to SSCF. Finally, for Scenario C (Table 3.6) also, the fermentation step was also classified with level 2 as only few industrial plants are using this procedure.

3.2.8.4 Preliminary Assessments

After the selection of scenarios, the identification of possible products, and the evaluation of the matureness of the technologies involved, preliminary mass and energy balances must be performed, as previously described, for proper comparison between scenarios.

Table 3.3 Matureness level at industrial scale for the used technologies in Scenario A

	Technologies/unit operations			
Scenario A	Milling	Hemicellulose removal	SHF/SSF	Separation
Matureness level	3	3	3	3

Table 3.4 Matureness level at industrial scale for the used technologies in Scenario A′

	Technologies/unit operations				
Scenario A′	Milling	Hemicellulose removal	SHF/SSF	Separation	Purification
Matureness level	3	3	3	3	2

Table 3.5 Matureness level at industrial scale for the used technologies in Scenario B

	Technologies/unit operations				
Scenario B	Milling	Hemicellulose removal	Purification	SSCF	Separation
Matureness level	3	3	3	2	3

SSCF simultaneous saccharification and co-fermentation

Table 3.6 Matureness level at industrial scale for the used technologies in Scenario C

	Technologies/unit operations					
Scenario C	Milling	Hemicellulose removal	Post-hydrolysis	Detoxification	SHF	Separation
Matureness level	3	3	3	3	2	3

Table 3.7 Experimental data used for heuristic analysis

Item	Units	Scenario			
		A	A′	B	C
Glucan recovery	%	90	90	90	90
Hemicellulose recovery	%	30	30	30	30
Cellulose pre-liquefaction	%	80	80	80	80
Hemicellulose pre-liquefaction	%	70	70	70	70
Ethanol yield (SHF)	g/g Glc	0.51	0.51	–	0.51
Ethanol yield from glucose (SSCF)	g/g Glc	–	–	0.51	–
Ethanol yield from xylose (SSCF)	g/g Xyl	–	–	0.41	–
Fermentation efficiency	%	90	90	90	90
Glucose assimilation	%	100	100	100	100
Lignin recovery (AH[a])	%	85	85	85	85
Lignin recovery (SHF)	%	90	90	90	90
Lignin sep. efficiency	%	100	100	100	100
XOS yield	%	60	60	60	–
XOS recovery	%	–	60	60	–
Post-hydrolysis yield	%	–	–	–	95
Xylose assimilation	%	–	–	–	95
Xylitol yield	%	–	–	–	51
Xylitol recovery	%	–	–	–	90
Steam for heating	ton/ton	1.0	1.0	–	–
Steam for pre-treatment	ton/ton	0.25	0.25	0.25	0.25
Steam for post-hydrolysis	ton/ton	–	–	–	0.1
Ethanol purity	%	99.5	99.5	99.5	99.5

[a]*AH* autohydrolysis

Although this is a preliminary assessment, some experimental data must be applied to achieve more accurate conclusions. Table 3.7 presents the relevant experimental data required to determine the mass and energy balances in each scenario.

Taking into account the simplified flowsheets presented before, the mass balances were calculated and are presented in Tables 3.8, 3.9, 3.10, and 3.11, for scenarios A, A′, B, and C.

For the energy balances, the heating required for pre-treatment in all scenarios and for post-hydrolysis (scenario C) was considered, considering the data shown in Table 3.7.

Subsequently, a preliminary economic assessment shall be performed. Since the calculation of detailed capital investment costs is very time consuming, a simplification can be achieved by correlating reported CAPEX in literature for several biorefinery plants, with different capacities (Table 3.12 and Fig. 3.8). A polynomial correlation between these two variables can be adjusted and is represented by the Eq. (3.1) ($R^2 = 0.93$).

Table 3.8 Preliminary mass balance for Scenario A

Compounds (dry basis)	Streams (ton/year)							
	1	2	3&4	5	5*	6	7	8
Corn stover	30,000	30,000	–	–	-	–	–	–
Glucan	–	12,249	–	11,024	2205	2205	2205	–
Xylan	–	7044	–	2113	634	634	634	–
Arabinan	–	918	–	275	83	83	83	–
Lignin	–	5073	–	4312	4312	3881	3881	–
Others	–	4716	–	–	–	–	–	–
XOS	–	–	4777	–	1672	1672	–	1672
GlcOS	–	–	1225	–	–	–	–	–
Molasses	–	–	6002	–	–	–	–	–
Lignin-rich solid	–	–	–	–	7233	6802	6802	–
Glucose	–	–	–	–	9799	–	–	–
Ethanol	–	–	–	–	–	4498	–	4475

Table 3.9 Preliminary mass balance for Scenario A′

Compounds (dry basis)	Streams (ton/year)							
	1	2	3	4	5	5*	6	7	8
Corn stover	30,000	30,000	–	–	–	–	–	–	–
Glucan	–	12,249	–	–	11,024	2205	2205	2205	–
Xylan	–	7044	–	–	2113	634	634	634	–
Arabinan	–	918	–	–	275	83	83	83	–
Lignin	–	5073	–	–	4312	4312	3881	3881	–
Others	–	4716	–	–	–	–	–	–	–
XOS	–	–	4777	2866	–	1672	1672	–	1672
GlcOS	–	–	1225	–	–	–	–	–	–
Molasses	–	–	6002	–	–	–	–	–	–
Lignin-rich solid	–	–	–	–	–	7233	6802	6802	–
Glucose	–	–	–	–	–	9799	–	–	–
Ethanol	–	–	–	–	–	–	4498	–	4475

$$\text{Correlation for CAPEX vs.Plant Capacity : CAPEX} \\ = 0.5571 \times \text{Plant Capacity (ton/year)}^{0.4912} \quad (3.1)$$

Regarding OPEX, these will depend on the operating units considered for each scenario. Feedstock costs, operating costs of process units, and labour were the components considered for the OPEX calculation. Table 3.13 summarizes the OPEX estimates for processing 30,000 ton/year of corn stover for each scenario. In Table 3.13 are also presented the CAPEX costs for each scenario using the same annual amount of feedstock, which results in equal costs regardless the scenario

Table 3.10 Preliminary mass balance for Scenario B

	Streams (ton/year)						
Compounds (dry basis)	1	2	3	4	5	6	7
Corn stover	30,000	30,000	–	–	–	–	–
Glucan	–	12,249	11,024	2205	2205	2205	–
Xylan	–	7044	2113	634	634	634	–
Arabinan	–	918	275	83	83	83	–
Lignin	–	5073	4312	3881	3881	3881	–
Others	–	4716	–	–	–	–	–
XOS	–	–	4777	1433	1433	–	1433
GlcOS	–	–	1225	245	245	–	245
Lignin-rich solid	–	–	17,725	6802	6802	6802	–
Glucose	–	–	–	10,888	–	–	–
Xylose	–	–	–	5016	1003	1003	–
Ethanol	–	–	–	–	6471	–	6439

since the previously presented correlation was used, in which the CAPEX only depends on the scale.

Regarding preliminary economic assessment, Scenario B, in which hemicellulose and cellulose streams that are obtained from biomass pre-treatment are processed together, leads to lower OPEX due to the absence of hemicellulose fraction independent valorisation. On the other hand, Scenario A and A′ have higher OPEX due to the hemicellulose fraction separation, being the latter higher due to the xylo-oligosaccharides valorisation. Scenario C, due to the post-hydrolysis step presents the highest OPEX among the assessed scenarios.

3.2.8.5 Process Scale and Scenario Selection

After concluding the preliminary assessments, the most promising scenario and the most adequate scale must be selected based on process economic feasibility, along with the previously referred items. The economic feasibility, as described above, is assessed by determining the NPV versus process scale. For the NPV calculation, the revenues as well as some economic factors (e.g., interest rate, plant lifetime) shall be taken into account. The data used for the preliminary assessment is summarized in Table 3.14. These data are based on feedstock costs including transport. Products' market prices and financial parameters were also conservatively estimated, based on diverse data sources (see below).

Figure 3.9 shows the NPV variation with the process scale (within the available feedstock amount) for the assessed scenarios. One can observe that Scenario A and Scenario B are not economically viable (NPV < 0) for any scale, while Scenario A′ is viable for any scale and Scenario C for scales higher than 40,000 ton/year of corn stover.

After concluding all the steps of the heuristic analysis, one can conclude that Scenario A′ and Scenario C are the most promising pathways for the corn stover-based biorefinery. Nonetheless, due to high added value of xylo-oligosaccharides

Table 3.11 Preliminary mass balance for Scenario C

Compounds (dry basis)	Streams (ton/year)									
	1	2	3	4	5	6	7	8	9	10
Corn stover	30,000	30,000	–	–	–	–	–	–	–	–
Glucan	–	12,249	–	–	–	11,024	2205	2205	2205	–
Xylan	–	7044	–	–	–	2113	634	634	634	–
Arabinan	–	918	–	–	–	275	275	275	275	–
Lignin	–	5073	–	–	–	4312	3881	3881	3881	–
Others	–	4716	–	–	–	–	–	–	–	–
XOS	–	–	4226	–	–	–	–	–	–	–
GlcOS	–	–	1225	–	–	–	–	–	–	–
Lignin-rich solid	–	–	–	–	–	–	6995	6995	6995	–
Xylose	–	–	–	4563	228	–	1900	1900	–	1900
Xylitol	–	–	–	–	1990	–	–	–	–	–
Glucose	–	–	–	1293	–	–	9799	–	–	–
Ethanol	–	–	–	–	–	–	–	4498	–	4475

Table 3.12 Capital investment and ethanol volume production of biorefinery plants reported in literature

Plant	Technology used		Production		CAPEX (M. USD)	References
	Pre-treatment	Fermentation	Feedstock (Mton/ year)	Ethanol (mil L/ year)		
Clariant	Uncatalyzed Steam Explosion	SSCF	4.5	1.3	34.2	Clariant (2017)
CIMV	Organosolv	SSCF	9.0	1.1	68.3	Delmas (2015)
BioGasol	Steam Explosion	SSCF	27.0	7.0	61.0	*BioGasol* (2017)
Inbicon	Autohydrolysis	SSF/SSCF	30.0	5.4	78.1	Persson (2013)
Biochemtex (Crescentino)	Uncatalyzed Steam Explosion	n/a	270.0	50.0	183.0	*Betarenewables* (2017)
POET-DSM	Acid-catalyzed Steam Explosion	SSCF	285.0	75.0	298.9	*POET-DSM* (2017)
Maabjerb Energy Center	n/a	n/a	300.0	80.0	292.8	*MEC* (2017)
Abengoa (Hugoton Plant)	Acid-catalyzed Steam Explosion	SSCF	350.0	94.0	378.2	ABENGOA (2013)
GRANBIO	Uncatalyzed Steam Explosion	SSCF	400.0	82 0.0	323.3	GranBio (2017)

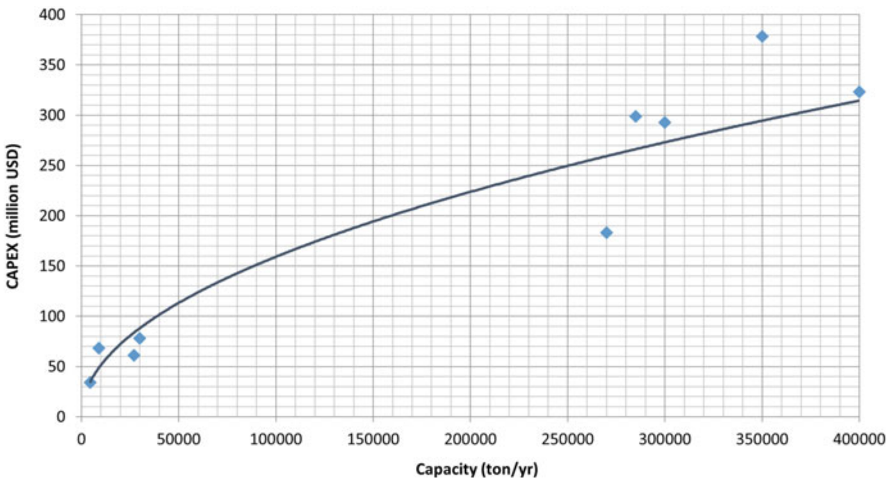

Fig. 3.8 Variation of capital investment costs with plant capacity, according to literature data

and its emerging market as prebiotics (Samanta et al. 2015), Scenario A′ is the most adequate route to assess in detail.

Following, the selected scenario shall be modelled using software-based tools for process engineering, for detailed mass and energy balances and equipment mapping, and consequently, a complete techno-economic analysis. Subsequently, an environmental assessment shall follow to validate the biorefinery sustainability.

3.3 Detailed Process Design and Simulation

The integrated corn stover (LCB)[3] and swine manure (ADB)[4] based biorefinery was simulated using Aspen Plus v10.0 (Aspen Technology, Inc., USA) to establish the requirements for feedstock, utilities, and energy. Physico-chemical properties of cellulose, hemicellulose, lignin, enzyme, and yeast were based on the NREL database (Wooley and Putsche 1996). The Non-Random Two Liquids (NRTL) thermodynamic model was used for the simulation of the behaviour of the liquid phases. The Hayden O'Connell equation of state was selected to represent the vapour phase (Quintero et al. 2013). The simulation was run based on product concentrations and yields from LNEG experimental data and from literature.

The flowsheet of the corn stover/swine manure integrated biorefinery is shown in Fig. 3.10, and it is divided into nine distinct sections: (1) Drying and milling; (2) Pre-treatment; (3) Enzymatic hydrolysis; (4) Fermentation; (5) Bioethanol

[3] LCB—lignocellulosic biorefinery.

[4] ADB—anaerobic digestion biorefinery.

Table 3.13 Example of preliminary OPEX estimates for the assessed scenarios for a scale of 30,000 ton/year

Scenario A	ton/year	Price (USD/ton)	Annual total (M.USD/year)
1. Feedstock			
Corn stover	30,000.0	54.9	1.65
Enzymes		185.5[a]	0.83
2. Operating costs			
Distillation	4475.3	79.3	0.35
Pre-treatment (heating)	37,500.0	12.2	0.46
Drying/evaporation	146,768.1	12.2	1.79
3. Labour			
Personnel costs			0.85
Total OPEX (Scenario A) (Million USD/year)			**5.93**
Total CAPEX (Scenario A) (Million USD)			**88.12**
Scenario A′	ton/year	Price (USD/ton)	Annual total (M.USD/year)
1. Feedstock			
Corn stover	30,000.0	54.9	1.65
Enzymes		185.5	0.83
2. Operating costs			
Distillation	4475.3	79.3	0.35
Pre-treatment (heating)	37,500.0	12.2	0.46
Purification (XOS)	156,002.1	9.8	1.52
Drying/evaporation	78,001.1	12.2	0.95
3. Labour			
Personnel costs			0.85
Total OPEX (Scenario A′) (Million USD/year)			**6.62**
Total CAPEX (Scenario A′) (Million USD)			**88.12**
Scenario B	ton/year	Price (USD/ton)	Annual total (M.USD/year)
1. Feedstock			
Corn Stover	30,000.0	54.9	1.65
Enzymes		185.5	1.19
2. Operating costs			
Distillation	6438.8	79.3	0.51
Pre-treatment (heating)	37,500.0	12.2	0.46
3. Labour			
Personnel costs			0.85
Total OPEX (Scenario B) (Million USD/year)			**4.66**
Total CAPEX (Scenario B) (Million USD)			**88.12**
Scenario C	ton/year	Price (USD/ton)	Annual total (M.USD/year)
1. Feedstock			
Corn Stover	30,000.0	54.9	1.65
Enzymes		185.5	0.83
2. Operating costs			
Distillation	4475.3	79.3	0.35
Pre-treatment (heating)	37,500.0	12.2	0.46

(continued)

Table 3.13 (continued)

Scenario C	ton/year	Price (USD/ton)	Annual total (M.USD/year)
Acid hydrolysis (H_2SO_4)	1500.0	104.9	0.16
Post-hydrolysis treatment	12,000.0	12.2	0.15
Neutralization ($Ca(OH)_2$)	2268.4	85.4	0.19
Xylitol prod. and purif.	1989.5	1509.1	3.00
3. Labour			
Personnel costs			1.28
Total OPEX (Scenario C) (Million USD/year)			**8.07**
Total CAPEX (Scenario C) (Million USD)			**88.12**

[a]Per ton of ethanol produced

Table 3.14 Market prices, feedstock availability, and economic factors considered for the preliminary economic feasibility assessment

Market prices[a]	USD/ton	Feedstock (corn stover)	ton/year
Feedstock	54.90	Minimum	30,000
Ethanol	732.00	Maximum	100,000
Lignin	54.90	**Economic factors**	
Pentose molasses	164.70	Payback period (years)	5
XOS	4270.00	Interest rate	0.05
Xylitol	4392.00	Plant lifetime (years)	20

[a]Estimates

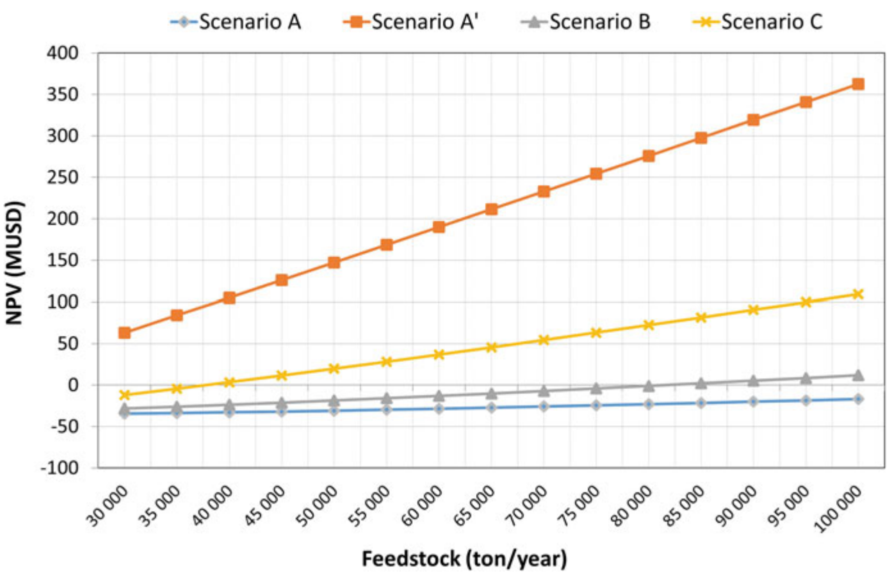

Fig. 3.9 Net present value versus the amount of processed feedstock for each scenario assessed

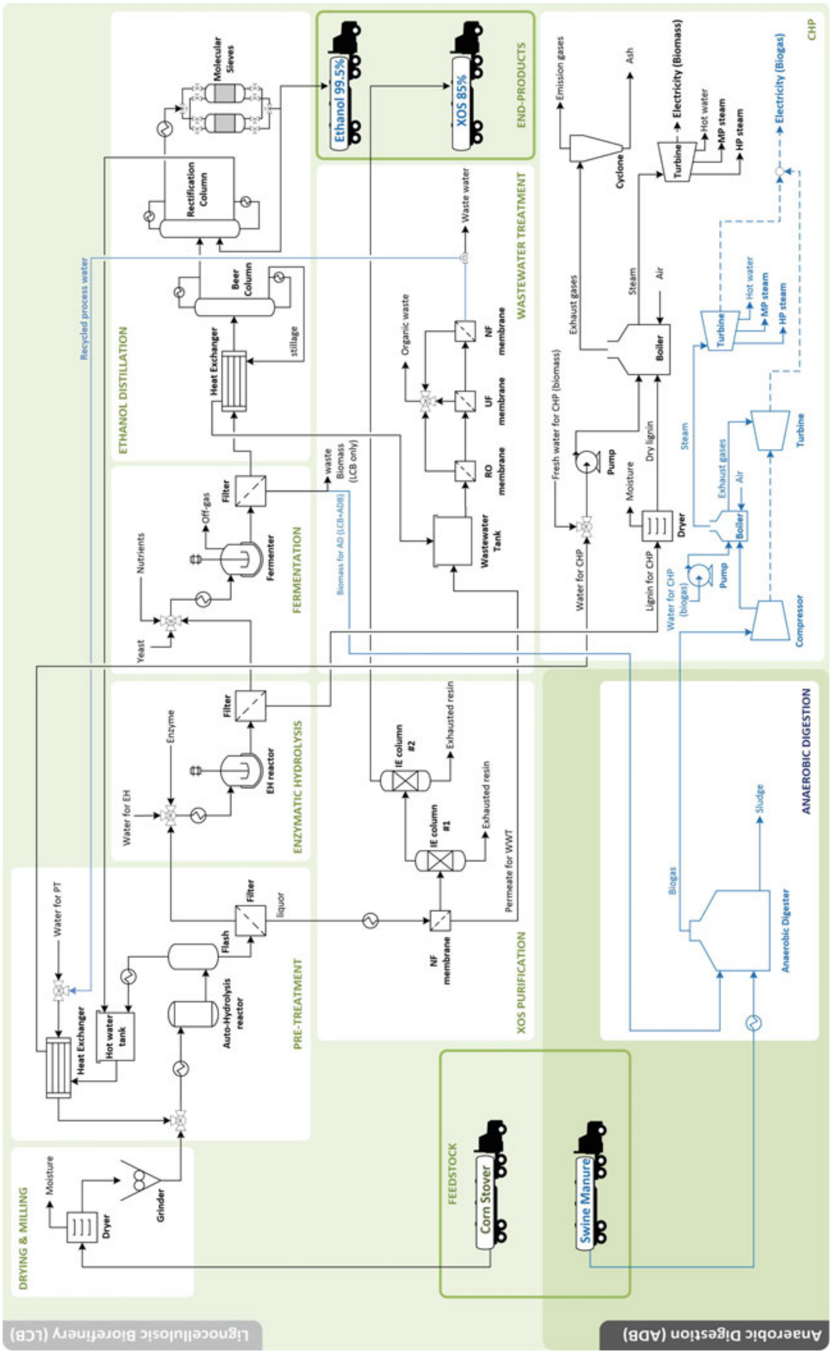

Fig. 3.10 Flowsheet scheme of the LCB and ADB for the selected scenario

Table 3.15 Autohydrolysis reactions and conversions

Reaction	Fractional conversion of component	Fractional conversion	References
Cellulose + H_2O → Glucose	Cellulose	0.024	Moniz (2014)
Cellulose → GlcOS	Cellulose	0.035	Moniz (2014)
Cellulose → HMF + $2H_2O$	Cellulose	0.002	Moniz (2014)
Xylan + H_2O → Xylose	Xylan	0.030	Moniz et al. (2013)
Xylan → XOS	Xylan	0.560	Moniz et al. (2013)
Xylan → Furfural +$2H_2O$	Xylan	0.016	Moniz et al. (2013)
Arabinan + H_2O → Arabinose	Arabinan	0.317	Moniz et al. (2013)
Arabinan → AOS	Arabinan	0.285	Moniz et al. (2013)
Acetate → Acetic Acid	Acetate	0.307	Moniz et al. (2013)
Lignin → Soluble Lignin	Lignin	0.150	Moniz et al. (2013)

GlcOS gluco-oligosaccharides, *XOS* xylo-oligosaccharides, *AOS* arabino-oligosaccharides

distillation and dehydration; (6) Xylo-oligosaccharides purification; (7) Wastewater treatment; (8) Anaerobic digestion, and (9) Combined Heat and Power generation.

3.3.1 Process Modelling

As available feedstock, 100,000 ton/year of corn stover was considered [dry weight basis: 40.2% of cellulose, 28.5% of hemicellulose, 20.8% of lignin, 2.9% protein and 1.5% of extractives] and 125 m^3/day of swine manure with 5% solids was also taken into account for the simulation procedure. Operation conditions and yields used as process parameters are described in the following sections.

3.3.1.1 Drying and Milling

First, corn stover is air-dried from an initial moisture of 20% to a final moisture of 10%. The lignocellulosic biomass is then milled (to particles below 6 mm) using a crusher.

3.3.1.2 Pre-treatment

Milled corn stover is conveyed to a hydrothermal pre-treatment (autohydrolysis) step for hemicellulose removal. The autohydrolysis is carried out using high-pressure steam (autogenous pressure of 19 bar at 210 °C) in a steam to solid ratio of 8:1. The considered hydrolysis reactions and conversions are presented in Table 3.15.

Upon completion of the autohydrolysis process, the solid and liquid fractions are separated. The liquid fraction (liquor) is subjected to a purification step for xylo-oligosaccharides recovery. The solid fraction is conveyed to the enzymatic hydrolysis step.

3.3.1.3 Enzymatic Hydrolysis

A separate hydrolysis and fermentation system was chosen. As previously referred, the solid fraction is recovered after pre-treatment and undergoes an enzymatic hydrolysis (EH) process. EH is run at 50 °C using Cellic CTec2® (Novozymes) at an enzyme loading of 20 mg g^{-1} of cellulose, and a total solid loading of 20% for 72 h (NREL 2011). The considered EH reactions and conversions are presented in Table 3.16.

3.3.1.4 Fermentation

Afterwards, the temperature is cooled to 32 °C in order to enable the fermentation step, where 1 g_{DW} L^{-1} (10 vol% of production vessel size) of *Saccharomyces cerevisiae* is used to inoculate the mixture. After 24 h from inoculation, a yield of 0.48 $g_{ethanol}$ $g_{glucose}{}^{-1}$ is obtained (Gírio and Fonseca 2015). The considered reactions for this step are presented in Table 3.17.

3.3.1.5 Ethanol Distillation and Dehydration

At the end of the fermentation, the broth is conveyed to the ethanol recovery section. This contains two distillation columns and one molecular sieve. The first column, called the beer column, takes ethanol concentration up to 60 wt% in the distillate, while the stillage (column bottoms) is conveyed to the wastewater treatment section after pre-heating the beer column feed. The second column, called rectification column, ethanol is to bring up to the azeotrope (93 wt%), while the column bottoms are sent to a hot water collector to pre-heat the water before the pre-treatment, and then sent to CHP for steam generation. In order to go beyond the azeotrope, the ethanol stream is sent to a molecular sieve until reaching a concentration of 99.5 wt% (fuel grade).

3.3.1.6 Xylo-Oligosaccharides Purification

The oligomers-rich liquor from pre-treatment undergoes a purification step with membranes. Firstly, the stream is cooled down to 90 °C and then goes through a

Table 3.16 Chemical reactions and fractional conversions considered for the enzymatic hydrolysis step

Reaction	Fractional conversion of component	Fractional conversion	References
Cellulose + H_2O → Glucose	Cellulose	0.80	Gírio and Fonseca (2015)
Xylan + H_2O → Xylose	Xylan	0.70	Gírio and Fonseca (2015)

Table 3.17 Chemical reactions and fractional conversions considered for the ethanologenic fermentation step

Reaction	Fractional conversion of component	Fractional conversion	References
Glucose $\rightarrow$ 2Ethanol + $2CO_2$	Glucose	0.950	NREL (2011)
Glucose + $2H_2O$ $\rightarrow$ 2Glycerol + O_2	Glucose	0.004	NREL (2011)
Glucose + $2CO_2$ $\rightarrow$ 2Succinic Acid + O_2	Glucose	0.006	NREL (2011)
Glucose + $0.0208SO_4^{2-}$ + $1.3705NH_4^{+}$ $\rightarrow$ 5.9603*S. cerevisiae* + $3.7945H_2O$	Glucose	0.020	NREL (2011)

nanofiltration membrane, followed by two subsequent ionic exchanging steps to reach xylo-oligosaccharides with 85% purity (Vegas et al. 2006, 2008).

3.3.1.7 Wastewater Treatment

The relevant wastewater streams, namely the permeate from the xylo-oligosaccharides purification, and the stillage from ethanol distillation, are mixed together. This mixed stream presents a low chemical oxygen demand (COD), and hence neither anaerobic nor aerobic digestion are suitable for its treatment. Thus, this stream is processed through membrane technology-based system comprising reverse osmosis, ultra-filtration, and nanofiltration to separate sugars, organics, and microorganisms from water. This allows a 90% recovery of the water back into the process. The remaining 10% are purged from the system.

3.3.1.8 Anaerobic Digestion

Spent yeast and swine manure undergoes a pre-heating process to reach 32 °C before being fed into the anaerobic digester, which is run at atmospheric pressure with a residence time of 30 days. The biogas (CH_4 and CO_2) yields assumed in the simulation process are presented in Table 3.18.

3.3.1.9 Combined Heat and Power Generation

The residual lignin obtained after the filtration of liquefaction (enzymatic hydrolysis) broth is sent to the power and heat generation section (CHP). After being dried until 5% moisture, it is fed into a boiler (1540 °C) for the production of high-pressure steam (HP, 24 bar), medium-pressure stream (MP, 7 bar), and hot water, as well as electricity. Table 3.19 presents the combustion reactions for lignin as well as for the

Table 3.18 Conversions considered for the anaerobic digestion reactor

Component	Yield (mass fraction)	Reference
CH_4	0.56	LNEG experimental data
CO_2	0.24	LNEG experimental data
Non-converted sludge	0.10	LNEG experimental data

Table 3.19 Chemical reactions and fractional conversions considered for the CHP section

Reaction	Fractional conversion of component	Fractional conversion	Ref.
Lignin + $10.125O_2 \rightarrow 7.3CO_2 + 6.95H_2O$	Lignin	1	Wooley and Putsche (1996)
Cellulose + $6O_2 \rightarrow 6CO_2 + 5H_2O$	Cellulose	1	Wooley and Putsche (1996)
Xylan + $5O_2 \rightarrow 5CO_2 + 4H_2O$	Xylan	1	Wooley and Putsche (1996)

residual hemicellulose and cellulose. The biogas from the Anaerobic Digestion is compressed up to 16 bar before being burned in a second boiler (2170 °C) to also generate HP, MP, hot water, and electricity.

3.3.2 LCB Only

For comparison reasons, a LCB-only scenario was also modelled. Under this scenario, the generated lignin is not enough to fulfil the process energy (electricity) needs by burning it in CHP, thus there is no electricity surplus. A detailed flowsheet for this scenario is represented in Fig. 3.11.

3.3.3 Results

Table 3.20 summarizes the mass balances obtained from the Aspen Plus model for the selected scenario, while Table 3.21 presents the energy balances. One can observe that by processing 100 kton/year of lignocellulosic residues (corn stover), ca. 12 kton/year of bioethanol together with ca. 8.3 kton/year of high purity xylo-oligosaccharides are produced. Regarding the utility needs in energy balances, a high amount of high-pressure steam is required for the pre-treatment and cooling water for the ethanol recovery. However, the integration with ADB leads to an electricity generation surplus that can be sold, for higher revenues, to the grid.

3.4 Techno-Economic Assessment

3.4.1 Methodology

The capital (CAPEX) and operating costs (OPEX) estimates were obtained using the Aspen Economic Analyzer tool (v8.4). For the calculations, a project lifetime of 20 years was considered based on the reports for most industrial chemical processes (Peters et al. 2003; *Trading Economics* 2017), and the straight-line depreciation method was applied. All economic parameters used in this assessment are related to Portuguese context, such as cost of raw materials, income tax, labour, product price, etc. More specifically, it was considered an income tax value of 21% (corporate tax in Portugal), and an annual interest rate of 2% (current rate for Portugal is around 0, thus a more conservative value was taken into account). Table 3.22 presents the economic data for raw material, products, and utilities.

The economic viability of the selected biorefinery was evaluated taking into account the Net Present Value (NPV). Following the *six-tenths-factor rule*, Eq. (3.2) (Peters et al. 2003), the influence of the process scale (amount of Corn Stover to be processed, up to 100 kton/year—maximum available amount in Chamusca region) was also assessed. This analysis can help to decide which range of processing capacity is the most adequate for positive profitability margins.

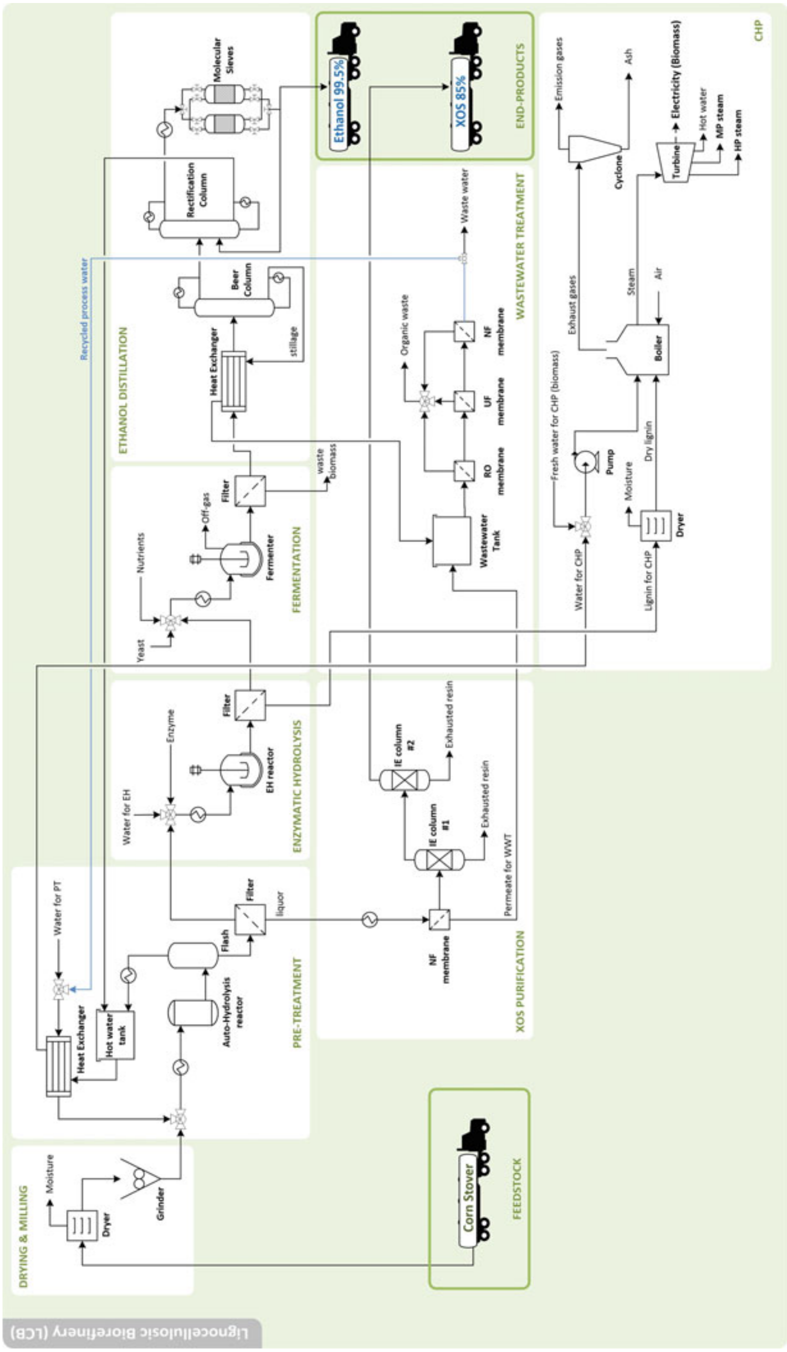

Fig. 3.11 Flowsheet scheme of the LCB (only) for the selected scenario

Table 3.20 Mass balances for the assessed biorefinery scenario obtained from process simulation

Inputs	ton/year	Outputs	ton/year
Corn stover	100,000	Ethanol (99.5%)	12,008
Swine manure	46,482	XOS (85%)	8345
Water (pre-treatment)	56,939	Moisture	18,758
Water (EH)	138,491	*Off-gas* ferm.	11,807
Nutrients	1376	Gas emissions	1,567,470
Yeast	25,857	Ash	2901
Enzyme	614	Organic waste	18,819
Air CHP (biogas)	716,848	Digestate	11,763
Air CHP (biomass)	769,728	Ion exchange waste	2866
Water (CHP)	600,980	Water purge	50,050

Table 3.21 Energy balances for the assessed biorefinery scenario obtained from process simulation

Utilities	ton/year
HP steam	64,300
MP steam	n/a
LP steam	10,364
Cooling water	2,633,785
Electricity (process) (MW)	30
Prod. CHP (biogas) (MW)	22
Prod. CHP (biomass) (MW)	28
Electricity process (surplus) (MW)	20

$$\text{Six-tenths-factor rule : Cost Equip.A} = \text{Cost Equip.B} \times \left(\frac{\text{Capacity A}}{\text{Capacity B}}\right)^{0.6} \tag{3.2}$$

3.4.2 Results

Figure 3.12 represents the impact of the plant capacity in the biorefinery profitability (NPV). It can be observed an increase of the NPV along with plant capacity, as expected. However, the amount of corn stover processed shall be higher than 40,000 ton/year for the plant to be economically viable. A payback period of ca. 2 years is expected when processing 100,000 ton/year of corn stover, being higher (ca. 9 years) for the lowest profitable scale (40,000 ton/year) which is almost half the lifetime considered for the project (20 years). The profitability is very sensitive to several variables, most noteworthy, products' market price, and the costs of the raw materials. Figure 3.13 presents the effect of a variation in these costs in the NPV of the project for the scenario of 100,000 ton/year of corn stover processed. One can conclude that the market price of XOS has the highest impact in process viability, since a reduction of ca. 35% of the considered selling price for XOS will make the process as economically non-viable (NPV < 0).

Table 3.22 Market prices of the raw material, utilities, and products

Compound	Value	Unit
Corn stover	52.10[a]	USD/ton
Swine manure	20.26[b]	USD/ton
Yeast	n.d.[c]	n.d.
Enzyme	176.10[d]	USD/ton
Ethanol	694.71	USD/ton
XOS	4052.48[e]	USD/ton
Xylitol	4168.26[e]	USD/ton
Electricity	0.051[f]	USD/MJ
Process water	0.36[g]	USD/m^3
Cooling water	0.13[h]	USD/m^3
High-pressure steam	9.86[i]	USD/ton
Mid-pressure steam	8.18[i]	USD/ton
Low-pressure steam	7.56[i]	USD/ton

[a]Price includes an estimate for transportation costs of corn stover from crops
[b]Price includes an estimate for transportation (between Chamusca and Lisbon, ca. 25 km)
[c]Not considered for the economic assessment
[d]Data for Novozymes Cellic® CTec3 (*Quora* 2017)
[e]Estimated based on current market prices for XOS-derivatives
[f]Price of electricity in Portugal (ERSE 2018)
[g]Average price in Portugal (*EPAL* 2017)
[h]Price estimated using correlations from (Ulrich and Vasudevan 2006)
[i]Estimates from Aspen Plus software

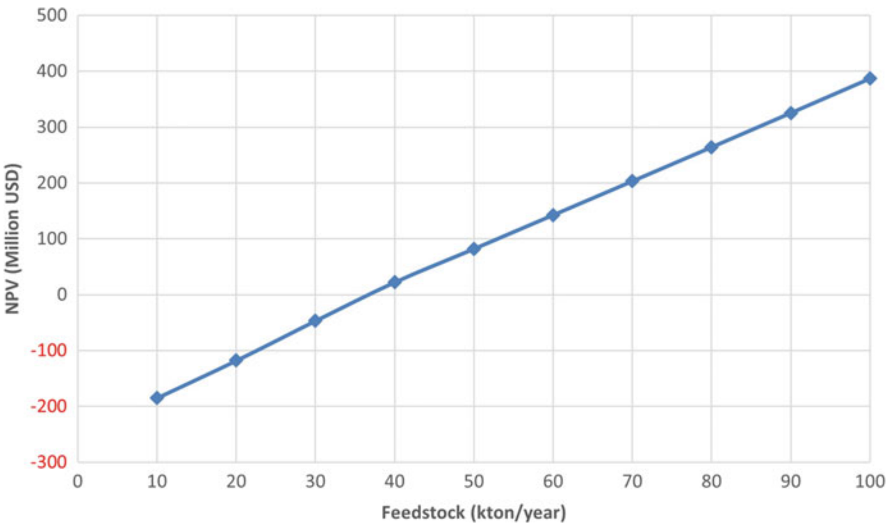

Fig. 3.12 Influence of the plant capacity in the Net Present Value for the LCB and ADB integrated biorefinery

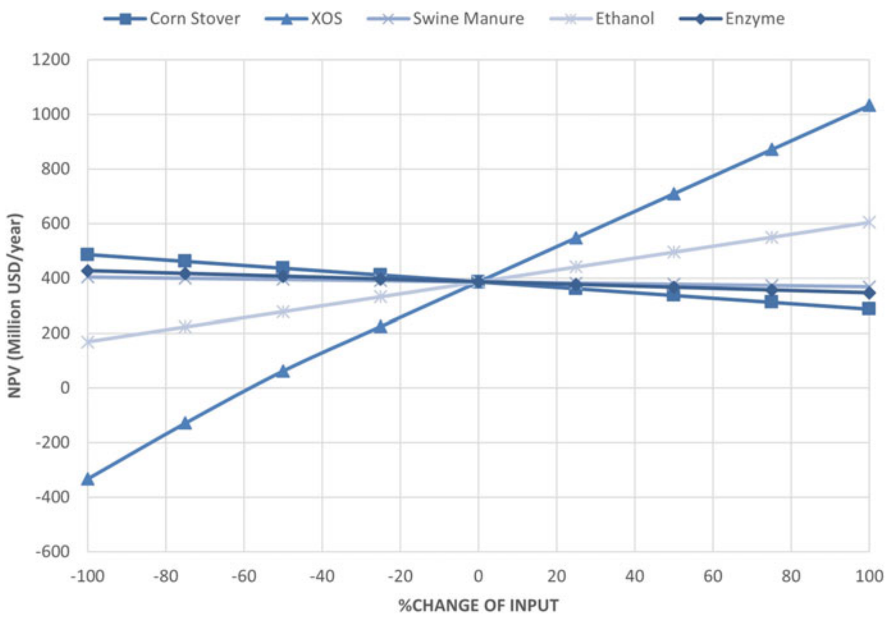

Fig. 3.13 Influence of the prices of raw materials and products in the NPV for the LCB and ADB integrated biorefinery

Table 3.23 Comparison between production costs and selling price per product of the integrated biorefinery (100,000 tons of corn stover per year)

Products	Production costs (USD/ton)	Selling price (USD/ton)	Profit margin (%)
Ethanol	448.06	950.00	112.0
XOS	1911.34	4052.48	
Electricity (USD/kWh)	0.03	0.06	

From the previous analysis, it is possible to calculate the production costs for the main biorefinery products. Table 3.23 shows the production costs for ethanol, xylo-oligosaccharides, and surplus electricity and the corresponding selling prices. A profit margin of ca. 112% is obtained for each product.

The effect of the ADB platform was assessed by the variation of different amounts of swine manure (within the available range—up to 46,480 ton/year). Figure 3.14 shows the CAPEX and the payback time variation with the amount of feedstock processed.

The process is still economically viable when using LCB only. The use of swine manure results in a higher CAPEX and generates an electricity surplus. By not using the ADB platform (swine manure = 0), a deficit of electricity is observed, and a need for electricity from the grid results in higher OPEX and lower revenues, which leads to higher payback times.

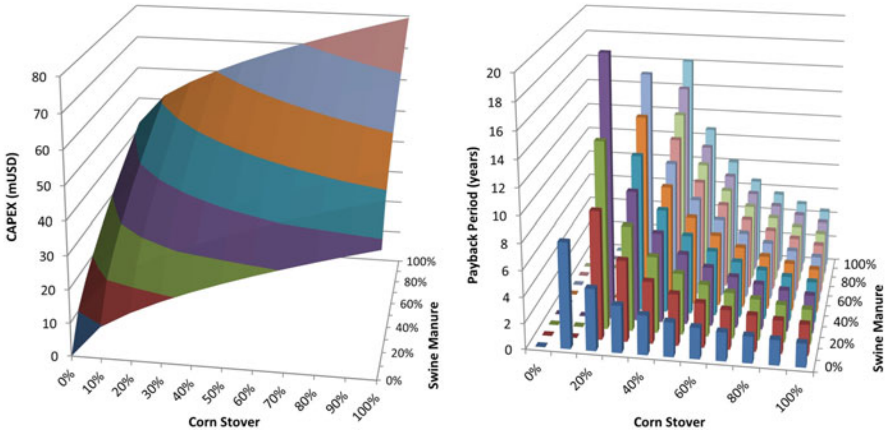

Fig. 3.14 Variation of the CAPEX (left) and payback period (right) with the amount of feedstock (corn stover and swine manure) used in the biorefinery

3.5 Life Cycle Assessment

3.5.1 Goal and Scope

For the selected scenario, the environmental impacts related to a biorefinery based in corn stover (CS) as dry biomass and swine manure (SM) as wet biomass were evaluated. For that purpose, a Life Cycle Assessment methodology was performed, following ISO 14040:2006.

The functional unit (FU) chosen for the assessment was 1 ton of lignocellulosic biomass, and the system boundaries are shown in Fig. 3.15, where a cradle-to-gate approach was followed (from corn stover and swine manure recollection to finished products at biorefinery gate). The system was divided in eight sub-systems: corn stover and swine manure recollection and transport (SS0a and SS0b, respectively), biomass pre-treatment (SS1), ethanol production (SS2), ethanol purification (SS3), XOS production (SS4), anaerobic digestion (SS5), wastewater treatment (SS6), and cogeneration (SS7).

3.5.2 Life Cycle Inventory

The system inventory data (inputs and outputs) were obtained from the simulation performed in Aspen Plus. The inventory data for background processes was taken from the Ecoinvent 3.5 database. Table 3.24 resumes the inventory data used for the LCA of this corn stover-based biorefinery. The environmental assessment was performed in SimaPro 9.1 also with Ecoinvent 3.5. The following categories were evaluated using ReCiPe Midpoint (H) methodology: GW—global warming

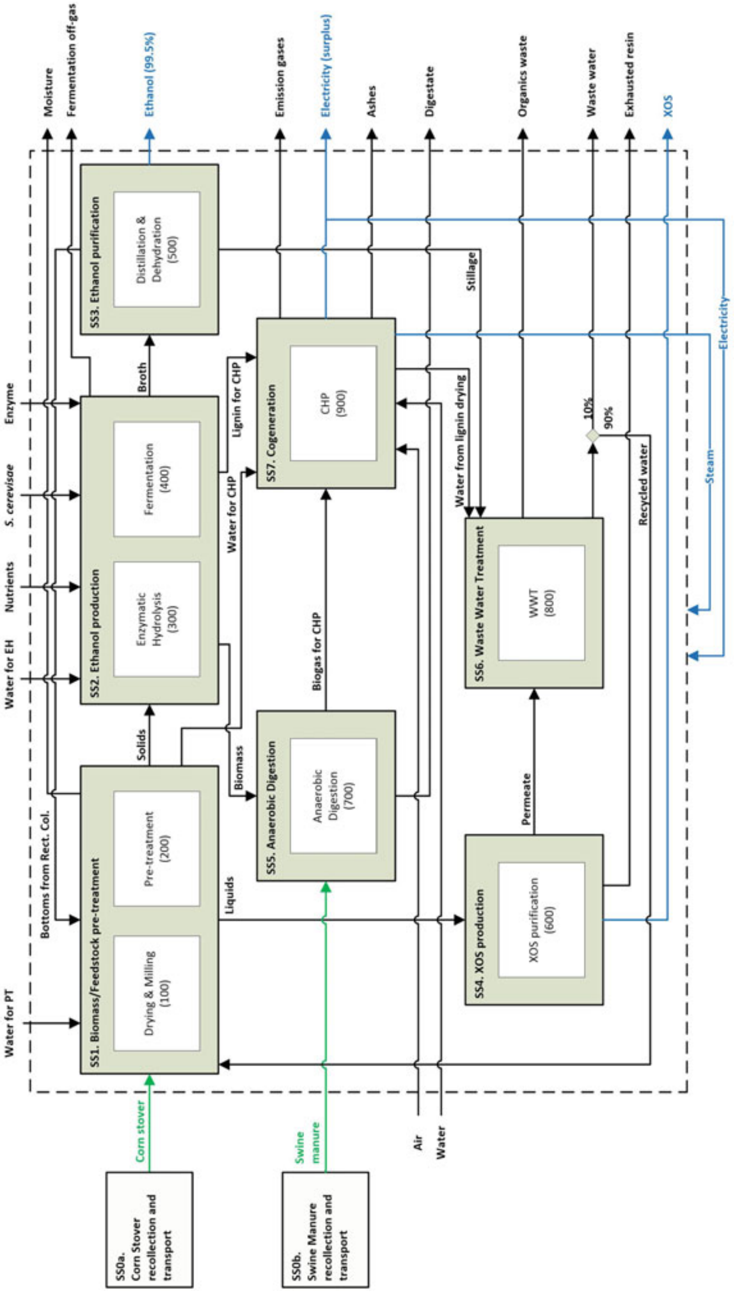

Fig. 3.15 Simplified flowchart of the corn stover/swine manure biorefinery system

Table 3.24 Inventory data for the corn stover (CS) and swine manure (SM) integrated biorefinery (values per FU = 1 ton lignocellulosic biomass)

Inputs			Outputs		
From the technosphere			Products		
CS (SS0)	1000	kg	Ethanol (99.5%)	122.46	kg
CS transport (SS0)	50.00	tkm	XOS (85%)	85.2	kg
SM transport (SS0)	21.85	tkm	Electricity	1.75	MWh
Water to SS1	339.06	kg	*Emissions to the air*		
Water to SS2	1384.99	kg	H_2O (SS1)	113.34	kg
Ammonium sulphate (SS2)	10.95	kg	CO_2 (SS2)	117.66	kg
Water in nutrients (SS2)	2.76	kg	O_2 (SS2)	0.45	kg
Yeast (SS2)	78.16	kg	H_2O (SS7)	1578.39	kg
Water in inoculum (SS2)	182.38	kg	CO_2 (SS7)	1297.98	kg
Enzyme (SS2)	6.14	kg	O_2 (SS7)	565.70	kg
SM (SS5)	464.85	kg	CO (SS7)	5.27	kg
Water for CHP (SS7)	1451.70	kg	N_2 (SS7)	9258.24	kg
From the environment			H_2 (SS7)	0.01	kg
Air for CHP (SS7)	12,099.49	kg	NO_2 (SS7)	0.26	kg
			NO (SS7)	51.04	kg
			Wastes to treatment		
			Ion exchanger sludge (SS4)	32.89	kg
			Digester sludge (SS5)	94.32	kg
			Chemical waste (SS6)	217.33	kg
			Ash to landfill (SS7)	29.01	kg

potential, SOD—stratospheric ozone depletion, FPMF—fine particulate matter formation, TA—terrestrial acidification; FE—freshwater eutrophication, ME—marine eutrophication, LU—land use, FRS—fossil resource scarcity, and, finally, WC—water consumption.

3.5.3 Environmental Characterization

The corn stover-based biorefinery aims to produce ethanol, xylo-oligosaccharides (XOS), and electricity. Due to this diversity of products, it is necessary to follow an allocation approach to distribute the environmental impacts associated to each product. Due to the different nature of the products (fuel, sugar, and energy), an economic allocation approach was followed. Table 3.25 presents the calculation of the allocation factors in this study, also including the results for mass allocation if electricity production is not taken into account.

In Table 3.26 are summarized the environmental impacts associated to each product, according to the economic allocation described above. Due to the market

Table 3.25 Calculation of the allocation factors

Product	Annual production (ton/year)	Market price		Revenues (M €/year)	Allocation (%)	
					Mass	Economic
Ethanol	12,009	820	€/ton	9.84	59.0	20.2
XOS	8345	3496	€/ton	29.18	41.0	59.9
Electricity (GWh/year)	175	0.08	€/kWh	9.66	–	19.9
Total	20,354	–		48.68	100	100

Table 3.26 Environmental impacts (values per FU = 1 ton lignocellulosic biomass)

Impact category	Total system	Ethanol	XOS	Electricity
GW (kg CO_2 eq)	412.75	83.38	247.24	82.14
SOD (kg CFC11 eq)	3.14×10^{-5}	6.34×10^{-6}	1.88×10^{-5}	6.24×10^{-6}
FPMF (kg PM10 eq)	12.13	2.45	7.27	2.41
TA (kg SO_2 eq)	31.12	6.29	18.64	6.19
FE (kg P eq)	0.30	0.06	0.18	0.06
ME (kg N eq)	3.23	0.65	1.94	0.64
LU (m^2a crop eq)	209.55	42.33	125.52	41.70
FRS (kg oil eq)	80.61	16.28	48.28	16.04
WC (m^3)	8.83	1.78	5.29	1.76

price of XOS, the highest contribution for each impact category is attributed to xylo-oligosaccharides.

Figure 3.16 presents the contribution of each subsystem to the environmental impacts. Regarding GW, the highest contributor is SS2 due to the use of yeast. Also, the enzyme and other processes included in SS2 have effect in this impact category. In other categories, such as TA, FE, ME and FPMF, is sub-system SS7 (cogeneration) that has the highest contribution, and this is mainly related to the combustion gases emissions.

3.5.4 Effect of the Use of Swine Manure (Wet Biomass)

As described above, in order to evaluate the effect of swine manure in the environmental sustainability of the integrated biorefinery, an alternative system was assessed by not considering the use of swine manure and consequently anaerobic digestion and biogas production. Figure 3.17 represents the process system where SS5 (Anaerobic Digestion) was removed.

Figure 3.18 shows a comparison between both systems (with and without swine manure). It was concluded that the use of swine manure as wet biomass has a positive effect in the biorefinery sustainability. This is due to the fact that when

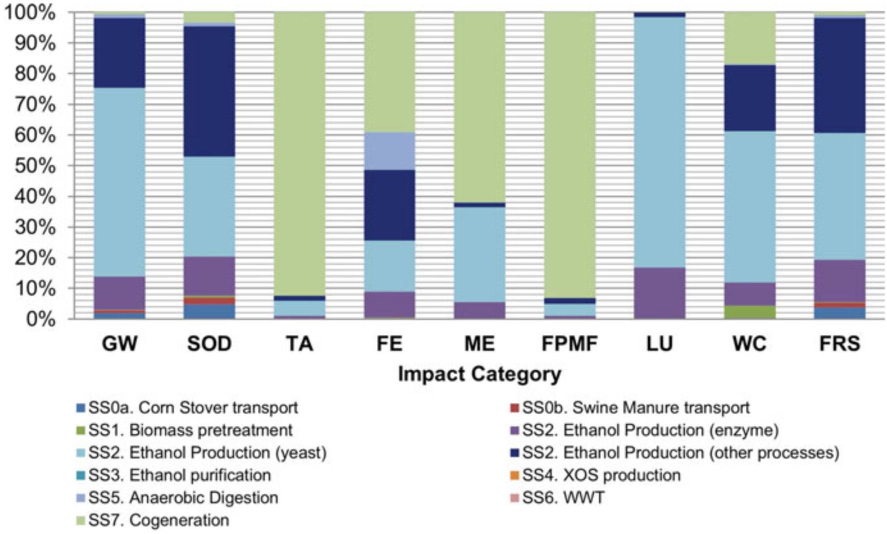

Fig. 3.16 Sub-systems contribution to the environmental impacts of the corn stover and swine manure based biorefinery

using swine manure, the production of biogas leads to an electricity surplus that can be sold to the grid. However, without swine manure there is the need of buying electricity from the grid and this has a negative effect in almost every impact category.

3.6 Legal Framework and Implementation Potential for Rural Areas

Technical, economic, and environmental viability of a new technological route could be inconsequential if there is no legal application for the developed project. In terms of biomass use, the Portuguese Government approved in 2017 four Decree-Laws that have direct impact in the use of biomass (lignocellulosic) residues aimed at reforming the forest sector. These are based on three main areas of intervention: forest territorial planning and management, property ownership, and finally, forest fire prevention and firefighting.

The referred decree-laws are:

- Decree-Law no. 64/2017, of 12 June, defines the rules for construction and operation of power plants to produce bioenergy (electricity and heat) from forest biomass by municipalities;
- Decree-Law no. 65/2017, of 12 June, that updates the Legal Framework for Forest Management, Intervention, and Zoning Plans, approved by Decree-Law no. 16/2009, of 14 January, aiming at a better clarification of the relation between

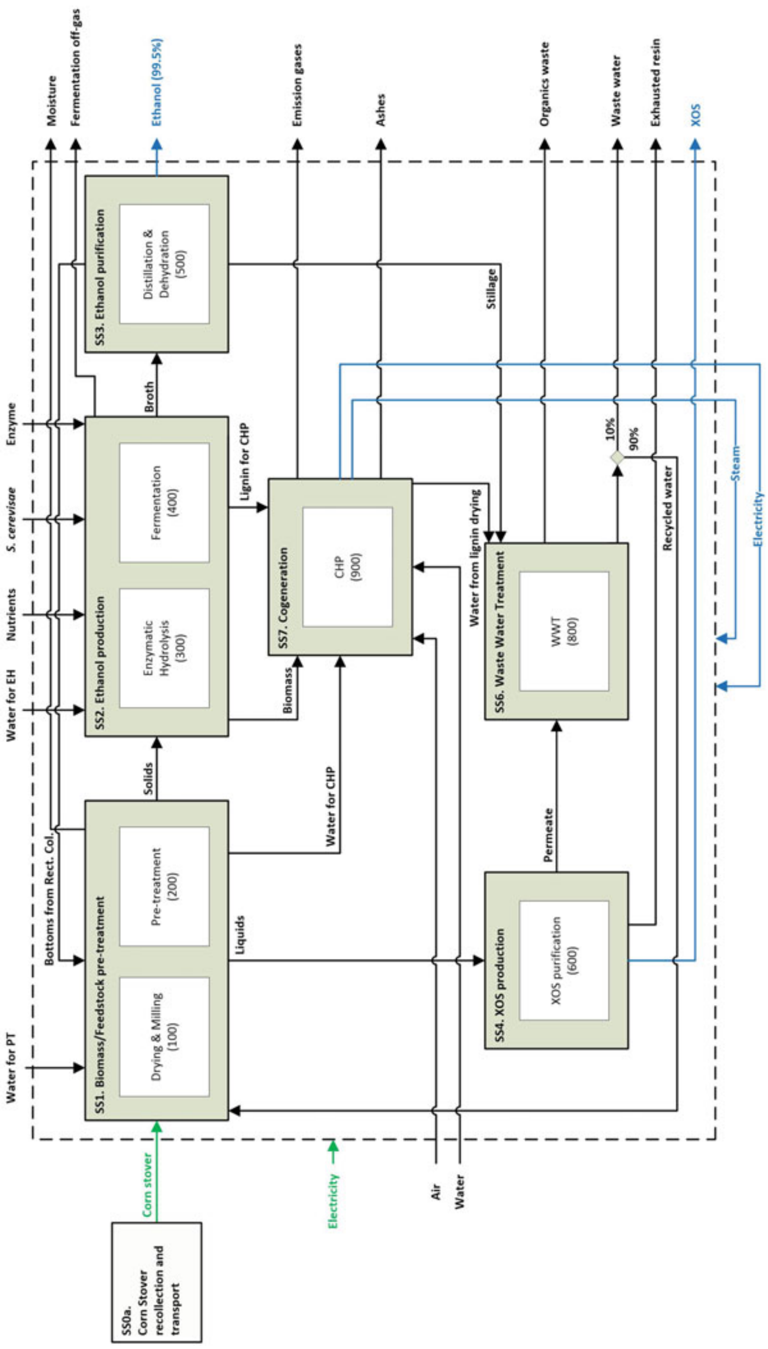

Fig. 3.17 Simplified flowchart of the corn stover (only) biorefinery system

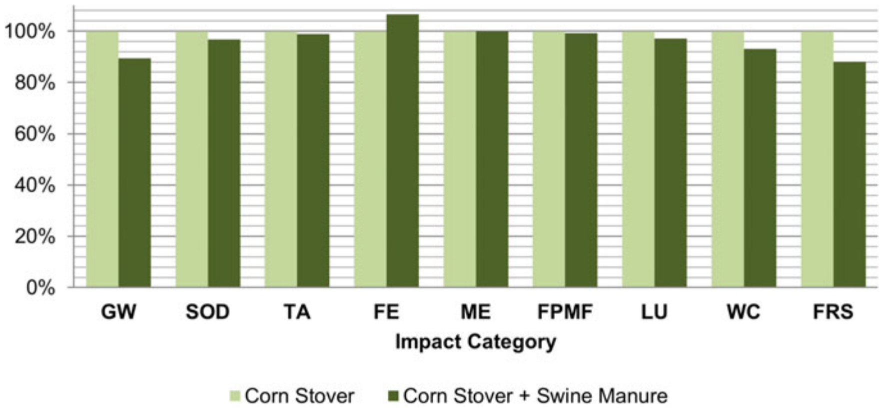

Fig. 3.18 Evaluation of the effect on the impact categories when using swine manure in the corn stover biorefinery

the regional forest zoning programmes and other programmes and plans for territorial management and a stronger protection of the forests by providing the authority to monitor compliance with such rules to the Institute for Nature Conservation and Forests (Instituto da Conservação da Natureza e Florestas) ("ICNF") ('Decreto-Lei n.º 65/2017' 2017);

- Decree-Law no. 66/2017, of 12 June, that sets forth the conditions and procedure for the recognition of forest management entities (agricultural cooperatives, private limited-liability companies or public limited-liability companies), who shall manage forest areas belonging to several owners in order to enhance their profitability by means of joint management ('Decreto-Lei n.º 66/2017' 2017);
- Decree-Law no. 67/2017, of 12 June, that updates the rules for creating forest intervention areas (ZIFs), approved by Decree-Law no. 127/2005, of 5 August, as amended, as well as enhances the creation of new ZIFs and improves the operation of existing ones ('Decreto-Lei n.º 67/2017' 2017).

Furthermore, regarding biorefineries, the Resolution of Council of Ministers no. 163/2017 ('Resolução do Conselho de Ministros n.º 163/2017' 2017) adopted the National Plan for the Promotion of Biorefineries (PNPB), under a policy of valuing the renewable energy sources and in the context of the use of the biomass, in accordance with the existing national potential. A strategy with the 2030 horizon is assumed to promote all types of advanced biorefineries in the country from biomass, so far not valued, waste or low economic value, such as agricultural and forestry waste biomass.

In line with the assessment reported in this chapter, Portugal has biomass residues available throughout the continental territory, with potential to be used in biorefineries and for energy purposes (electricity, heat, and advanced biofuels). Specifically, corn residues still have an untapped potential for the biorefinery concept. The integrated biorefinery concept (LCB and ADB) is an example of the application of circular bioeconomy, as the generated compost from the anaerobic digestion of swine manure can be used as a fertilizer for the corn cultivation. Nonetheless, it is important to notice that corn cultivation is seasonal, therefore an integrated biorefinery which can process more than one type of lignocellulosic biomass is more advantageous. The availability of different type of biomass residues in a certain radius can directly affect the profitability of the biorefinery.

Still, based on the referred legislation, one can conclude that the implementation of a corn stover/swine manure integrated small-scale biorefinery is very realistic in the short term, not only in the Portuguese territory but also all across Europe where different lignocellulosic residues and wet residues are available.

3.7 Conclusions

Valorization of all lignocellulosic biomass fractions is of extreme importance for the economic and sustainable viability of a biorefinery. The hemicellulose fraction, if valorized into oligosaccharides, shall be a possible way for the breakthrough of lignocellulosic-based biorefineries and its implementation.

Small-scale biorefineries can be economically viable if adapted to rural areas with suitable logistics and supply chains. Similar conclusions have already been achieved for a similar process by (Lopes et al. 2019), but in which the main product of the fermentation would be isobutene (in addition to the XOS obtained in the pre-treatment). A heuristic approach to evaluate the possible technological routes and the selection of feasible scenarios, followed by a detailed techno-economic analysis together with process simulation tools are useful for scale-up analysis and economic viability of biorefineries. Small-scale biorefineries can be environmentally sustainable depending on the products obtained, and subsequently the required operation units, along the whole value chain.

In a near future, it will be important to assess other types of residual biomass to overcome the issues of seasonality and availability (e.g., eucalyptus residues). Also, Social Impact Assessment on the various stakeholders (e.g., local community, agricultural producers, livestock producers, workers, etc.) for the implementation of a biofuels/bioproducts based biorefinery shall be addressed.

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