Modeling and Analysis

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Techno-economic and life-cycle assessments of small-scale biorefineries for isobutene and xylo-oligosaccharides production: a comparative study in Portugal and Chile

Tiago F. Lopes, Florbela Carvalheiro, Luís C. Duarte, and Francisco Gírio, Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Lisbon, Portugal
Julián A. Quintero, Department of Chemical Engineering, Universidad de Santiago de Chile, Santiago, Chile
Germán Aroca, School of Biochemical Engineering, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile

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Abstract: This work presents a comparative simulation study involving the techno-economic and environmental assessment of lignocellulosic-based small-scale biorefineries, integrated with a piggery waste-based anaerobic digestion platform (ADB), located in Portugal and Chile. Two main products are obtained: isobutene and xylo-oligosaccharides (XOS). The bioproduction of isobutene using a genetically engineered organism (*Escherichia coli*), coupled with the removal and purification of high added-value XOS, obtained after a feedstock hydrothermal pre-treatment, was evaluated. Two lignocellulosic agricultural wastes were used: corn stover in the Portuguese case study and wheat straw in Chilean case study. Both processes were simulated using the Aspen Plus modeling software tool, while the Aspen Process Economic Analyzer was used to carry out the economic evaluation. The simulation results were validated with experimental data from the laboratory and the literature. An economic assessment was performed considering the different locations of both biorefineries. A life-cycle analysis (LCA) was also applied to evaluate the differences in environmental impacts on both locations. The results showed that the isobutene / XOS biorefinery concept was economically viable in both Portugal and Chile, mainly due to the high market value of XOS. The biorefinery has lower production costs for isobutene and XOS (1 US$/kg of isobutene and 1.18 US$/kg of XOS) when located in Portugal, as compared with Chile (1.14

Correspondence to: Francisco Gírio, Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038 Lisbon, Portugal. E-mail: francisco.girio@lneg.pt

US$/kg of isobutene and 1.56 US$/kg of XOS). Conversely, it leads to less environmental impact when located in Chile: 48.8 $kg_{CO2eq.}/GJ_{isobutene}$, in comparison to 60.7 $kg_{CO2eq.}/GJ_{isobutene}$ in Portugal.

Supporting information may be found in the online version of this article.

Keywords: isobutene; XOS; advanced biofuels; biorefineries; process simulation; LCA

Introduction

Fossil fuel depletion, climate change, and global energy demands have given rise to a need to find suitable bio-substitutes for products currently obtained from fossil sources.[1] One way to do this is through the development of biorefinery processes for the production of biofuels and bioproducts with lower global warming potential (GWP). Biorefineries initially followed oil refineries by using a single feedstock with huge processing capacities to achieve the maximum economy of scale, but the opportunities for installing such biorefineries in most rural areas in Europe, Latin American countries, and even worldwide are scarce. Studies have revealed that the main bottlenecks are associated with high capital expenditure (CAPEX) and operating expenditure (OPEX), and very often the lack of a sustainable biomass supply at regional level.[2] Small-scale biorefineries have been proposed as a potential solution to overcome most of these challenges because, when located in rural areas, they can promote territorial economic cohesion and generate local jobs directly and indirectly.[3] Their small scale allows a reduction in the transportation costs of raw materials and intermediate products, and leads to a direct link between industry and the primary sector. Despite the strategic relevance of small-scale biorefineries, numerous technological and strategic challenges still hamper commercial development, namely the heterogeneity of the biomass resources for further processing.[4] For instance, in rural temperate and humid tropical regions, the majority of biomass resources are crop and food residues, animal and human waste, and agro-processing residues.

One way to take advantage of this heterogeneity is by combining two different biorefinery platforms: the biochemical platform transforming lignocellulosic feedstock into sugars and then into biofuels and / or added value chemicals, and the anaerobic digestion platform converting wet biomass into biogas.[5] Such a small-scale integrated biorefinery should be able to transform dry and wet biomass residues by means of different processes to produce an array of bioproducts, maximizing the resources, energy efficiency, and the environmental sustainability of the whole value chain.

In this work, a prototype small-scale biorefinery is proposed and evaluated in two different regional case studies. The biochemical platform pretreats agricultural residues by autohydrolysis, yielding a cellulose-rich pulp, and a liquor rich in oligomeric sugars; xylo-oligosaccharides (XOS), which are an emerging food additive used as prebiotic, are obtained as a high added-value product from this liquor.[6] The pulp is enzymatically hydrolyzed and the glucose syrup produced is fermented by an engineered strain of *Escherichia coli* under anaerobic conditions to produce isobutene (2-methylpropene), which is a precursor in several industrial applications, for example, Methyl tert-butyl ether (MTBE), Ethyl tert-butyl ether (ETBE), and isooctane, among others.[7] Secondary streams, such as residual cellulolignin solids and spent broth are used either for energy production in a combined heat and power plant (CHP) framework, or upgraded together with piggery waste in an anaerobic digestion platform to produce biogas.

The performance of the isobutene-producing biorefinery was evaluated by process modeling and simulation using software-based tools, as this is a useful methodology to ascertain process feasibility at scales larger than laboratory scale, such as pilot and industrial scales.[8–10]

This work also aims to evaluate the external factors influencing economic viability of this small-scale biorefinery, identifying the main factors affecting the sustainability of a similar biorefinery concept in two completely different geographical locations but having similar lignocellulosic feedstock (corn stover or wheat straw) and wet biomass residues (swine manure).

Methods

Biorefinery design

Feedstock and product selection criteria

Corn is the second largest cereal crop in Portugal, where particular conditions for its cultivation can be found (productivity up to 14 t ha^{-1}).[11] The main corn residue, corn stover, can account for up to 80%, by weight, of the produced corn and is mainly left in the field, where it takes a long time to degrade. Around 110 000 ha are dedicated to corn cultivation.[12] This production is mainly concentrated in certain Portuguese geographical areas, such as in Chamusca, Ribatejo region (ca. 100 km northeast from Lisbon).

Table 1 shows the composition of the corn stover analyzed in this work. The chemical characterization was performed using the methods described in Carvalheiro *et al.*[13] The cellulose content of corn stover is a suitable source of glucose, upon enzymatic hydrolysis, to be used for the production of advanced biofuels, while the high hemicellulose content is particularly interesting for the extraction of high-added value oligosaccharides.

In the Chamusca area, in the Portuguese case study, near to the maize fields, a pig farm was identified producing daily up to 125 m^3 of swine manure with 5% solid content.[14] Anaerobic digestion (AD) is an effective process to valorize this waste and to prevent environmental contamination resulting from pig farming practices. It produces a digestate that can be further used, either as fertilizer or biogas for electricity.

In Chile, wheat is the major cereal crop cultivated in the La Araucania region, where ca. 250 000 ha is dedicated to this crop, with productivity reaching up to 5.6 $t\,ha^{-1}$.[15] The straw can represent up to 45% of the whole plant and is usually burnt in the field. A small fraction of this residue is used for energy generation.

As with corn stover, the high content of polysaccharide in wheat straw as analyzed for this work (Table 1) also makes this biomass an interesting feedstock for the biorefineries, for the production of solvents and biofuels. The high hemicellulose content can also be exploited for the production of oligosaccharides. Similar to the Portuguese case, livestock farms located in the La Araucanía region produce around 120 m^3 of swine manure daily (data not published).

Process overview and design

Figure 1 shows a flowsheet of the proposed integrated biorefinery process. The process was divided into nine sections: (1) drying and milling, (2) pre-treatment, (3) enzymatic hydrolysis, (4) fermentation, (5) isobutene recovery, (6) xylo-oligosaccharide recovery, (7) wastewater treatment, (8) anaerobic digestion, and (9) combined heat and power.

Allowing for the availability of residues per region, 100 000 tonne per year of corn stover and 32 000 tonne per year of wheat straw were considered for the Portuguese and Chilean case studies, respectively. For both case studies, only a percentage of the total available amount of residue per region was selected, to secure soil carbon and quality. The daily maximum production of swine manure for each region was used for the calculations. The operating conditions and yields described below were used as process parameters.

(1) Drying and milling (DM)

Both corn stover and wheat straw are first dried with air. The initial moisture is 20% and the final moisture is 10%. Then the lignocellulosic biomass is milled in a crusher into particles of < 6 mm.

(2) Pre-treatment (PT)

The milled biomass undergoes a hydrothermal pre-treatment for hemicellulose fractionation. The autohydrolysis step is performed with high-pressure steam into an autogenous pressure of 19 bar at 210 °C, with a solids-to-steam ratio of 1:8.[13] Table 2 summarizes the hydrolysis reactions and conversions considered.

After this process, liquid and solid fractions are separated. The solid fraction proceeds into the enzymatic hydrolysis step while the liquid fraction (liquor) undergoes a purification step for XOS recovery.[16]

(3) Enzymatic hydrolysis (EH)

For the enzymatic hydrolysis step, a separate hydrolysis and fermentation (SHF) strategy was considered. Enzymatic hydrolysis is carried out at 50 °C using 20 $mg\,g^{-1}$ of cellulose of the new generation Cellic® CTec3 cellulase (Novozymes, Bagsvard, Denmark) at 20 wt% of total solids loading, which ensures a better performance than that reported by National Renewable Energy Laboratory (NREL) using a similar feedstock (corn stover) with a former generation enzyme (Cellic® CTec2).[17] The EH reactions and fractional conversions considered are summarized in Table 3. At the end of the hydrolysis (after 72 h by a conservative estimate), the lignin-rich solids are recovered by filtration and conveyed to CHP, whereas the glucose-rich stream is directed for fermentation.

(4) Fermentation (FERM)

Before fermentation, nutrients are added to the hydrolysate and the culture medium is sterilized at 121 °C. The temperature is then reduced to 32 °C to perform the fermentation step. A 10% inoculum, of engineered *E. coli* is used to seed the culture to an initial cell concentration of

Table 1. Composition of corn stover and wheat straw (in dry weight basis) considered in this work.

Feedstock	Composition (%)					
	Cellulose	Hemicellulose	Lignin	Protein	Extractives	Others
Corn Stover	40.2	28.5	20.8	2.9	1.5	6.1
Wheat Straw	36.8	25.9	19.0	0.3	14.5	3.5

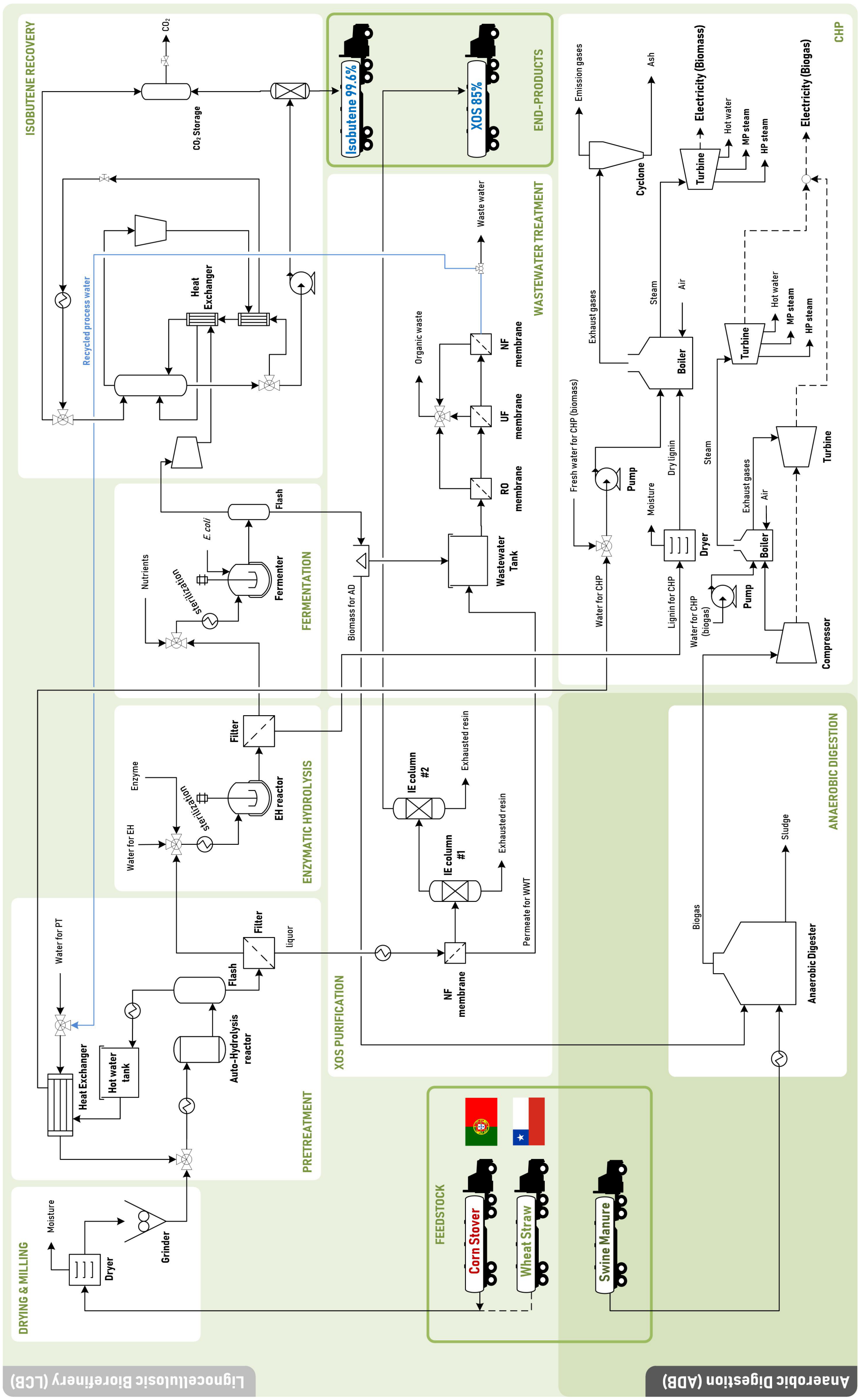

Figure 1. Flowsheet of isobutene and xylo-oligosaccharides production from lignocellulosic residues.

1 g DW L^{-1}.[7] The reactions and respective conversions for this step are summarized in Table 4.

(5) Isobutene recovery (ISO)

Bacterial fermentation produces an off-gas stream with a composition of about 2/3 carbon dioxide and 1/3 isobutene. This mixture is separated with a combination of cryogenic distillation and adsorption. Cryogenic distillation is accomplished in a vapor recompression column coupled to a refrigeration system to provide cooling at the condenser.[18] Vapor from the top of the column is compressed at 19 bar and used to provide the energy required in the reboiler and then expanded and sent to the condenser, which operates at 4 bar and −62 °C. Isobutene obtained from the bottom of the column reaches a purity of 90%wt. Pressure swing adsorption is used to reach the purity of 99.6% by a DD3R-zeolite molecular sieve.[19]

(6) Xylo-oligosaccharide recovery (XOS)

The oligomer-rich liquor from lignocellulosic biomass residues pre-treatment is recovered through combined nanofiltration and ion-exchange chromatography operation units. The stream is cooled down to 90 °C and nanofiltered. The permeate, is fractionated through two consecutive ion-exchange columns in order to reach a XOS stream with a DP range of 4–6 and a purity higher than 85%. The purification yields for each step were adapted from literature.[20,21]

(7) Wastewater treatment (WWT)

Wastewater streams (permeate from XOS purification) are recovered into a vessel. Due to the low Chemical Oxygen Demand (COD) of this wastewater mix, anaerobic, or aerobic digestion are not suitable for its treatment, thus the water is processed into three membrane systems (reverse osmosis, ultrafiltration, and nanofiltration) to separate sugars, organics, and microorganisms from water. Then, 90% of the water is recovered into the process (as water for pre-treatment) and the remaining 10% is purged from the system.

(8) Anaerobic digestion (AD)

The wet biomass, swine manure, undergoes a preheating process until it reaches 32 °C before entering the anaerobic digester, together with the spent broth from the bacterial fermentation step. The biogas yields (CH_4 and CO_2) considered for the simulation process are summarized in Table 5. The non-converted AD biomass sludge was also taken into account. The digester works at atmospheric pressure (1 bar) and 32 °C, with a residence time of 30 days.[14]

(9) Combined heat and power (CHP)

The lignin-rich solids from section (3), are dried until 5% moisture remains and are combusted at 1540 °C in a

Table 2. Chemical reactions and fractional conversions during pre-treatment step.

Reaction	Fractional conversion of component	Fractional conversion	Ref.
Cellulose + H_2O → glucose	Cellulose	0.024	26–29
Cellulose → glucoligomers (GlcOS)	Cellulose	0.035	26–29
Cellulose → HMF + 2 H_2O	Cellulose	0.002	26–29
Xylan + H_2O → xylose	Xylan	0.030	29
Xylan → xyloligomers (XOS)	Xylan	0.560	29
Xylan → furfural +2 H_2O	Xylan	0.016	29
Arabinan + H_2O → arabinose	Arabinan	0.317	29
Arabinan → araboligomers (AOS)	Arabinan	0.285	29
Acetate → acetic acid	Acetate	0.307	29
Lignin → soluble lignin	Lignin	0.150	30

Table 4. Biological reactions and fractional conversions during fermentation step.

Reaction	Fractional conversion of component	Fractional conversion	Ref.
0.175 Glucose +0.2 NH_4^+ → *E. coli* + 0.45 H_2O + 0.05 CO_2	Glucose	0.05	32
Glucose → Isobutene +2 CO_2 + 2 H_2O	Glucose	0.90	32
5 Glucose → 6 Acetone + 12 CO_2 + 12 H_2	Glucose	0.05	32
Xylose → 2 CO_2 + 2 H_2 + Acetone	Xylose	1.00	32

Table 3. Fractional conversions for enzymatic hydrolysis.

		Fractional conversion		
Reaction	Fractional conversion of component	Liquefaction	Saccharification	Ref.
Cellulose + H_2O → glucose	Cellulose	0.800	0.985	31
Xylan + H_2O → xylose	Xylan	0.700	0.856	31

Table 5. Component yields in anaerobic digestion reactor.

Component	Yield (mass fraction)	Ref.
CH_4	0.56	LNEG experimental data.[14]
CO_2	0.24	LNEG experimental data.[14]
Swine manure	0.10	LNEG experimental data.[14]
E. coli	0.10	LNEG experimental data.[14]

Table 6. Combustion reactions and fractional conversions in CHP section.

Reaction	Fractional conversion of component	Fractional conversion	Ref.
Lignin + 10.125 O_2 → 7.3 CO_2 + 6.95 H_2O	Lignin	1	22
Cellulose + 6 O_2 → 6 CO_2 + 5 H_2O	Cellulose	1	22
Xylan + 5 O_2 → 5 CO_2 + 4 H_2O	Xylan	1	22

boiler with 20% of excess O_2 for the production of high-pressure (HP) steam (24 bar), medium-pressure (MP) steam (7 bar), hot water, and electricity from steam expansion in a turbine. The combustion reactions for lignin, cellulose, and hemicellulose are summarized in Table 6. Furthermore, the biogas from AD is compressed to 16 bar before being burned in a boiler at 1967 °C, with 20% of excess O_2. The exhaust gases are expanded in a turbine to generate electricity while the generated steam inside the boiler is sent to a system similar to the one used for biomass and this produces HP and MP steam, and hot water.

Process simulation

Mass and energy balances were obtained by simulation using Aspen Plus v10.0 (Aspen Technology Inc., Bedford, Massachusetts, USA). The objective of this procedure was to determine the requirements for raw material, utilities and energy needs. The thermodynamic model used in the simulation was the non-random two liquids (NRTL) model. This analyzed the behavior of the liquid phase and the Hayden O'Connell equation of state was used to describe the vapor phase. For the simulation, the physical properties of lignocellulosic components and microorganisms (such as cellulose, hemicellulose, lignin, enzyme, and bacteria) were taken from the NREL database report.[22]

A vapor recompression distillation column model was adapted for the isobutene / CO_2 separation model.[18] A RadFrac column at 4 bar with no condenser, no reboiler, and with cryogenic convergence was modeled. For cryogenic distillation, a refrigeration cycle has to be taken into account; thus, the distillate vapor is re-compressed up to 19 bar and used for pre-heating the column feed, then it is expanded through an expansion valve to 4 bar. The CO_2 is recovered at the top of the column and isobutene with a purity of 99.6% is obtained at the bottom.

Techno-economic analysis

The capital and operating costs (CAPEX and OPEX, respectively) were calculated using the Aspen Economic Analyzer v.10.0. A 20-year lifetime process was assumed in line with similar industrial processes.[23] Equipment mapping adapted to the economic conditions of both countries (e.g., tax rate, interest rate, and wages, among others) was performed to determine both capital and operating costs including raw material, utilities, labor, and maintenance. The

Table 7. Market prices of the raw material, utilities, and products.

Compound	Value	Unit
Corn Stover	52.10[a]	US$/t
Wheat straw	35.00[b]	US$/t
Swine manure (Portugal)	20.26[c]	US$/t
Swine manure (Chile)	5.00[d]	US$/t
E. coli	n.d.[e]	—
Nutrients	n.d.[e]	—
Enzyme	176.10[f]	US$/t
Isobutene	2017.4[g]	US$/t
XOS	4052.48[h]	US$/t
Electricity (Portugal)	0.051[i]	US$/MJ
Electricity (Chile)	0.083[j]	US$/MJ
Process water	0.36[k]	US$/$m^3$
Cooling water	0.13[l]	US$/$m^3$
HP steam	9.86	US$/t
MP steam	8.18	US$/t
LP steam	7.56	US$/t

[a]Price includes an estimate for transportation costs of corn stover from crops.
[b]Price includes an estimate for transportation costs of wheat straw.
[c]Price includes an estimate for transportation (between Chamusca and Lisbon, ca. 25 km).
[d]Price includes an estimate for transportation (50 km).
[e]Not considered for the economic assessment.
[f]Data for Novozymes Cellic® CTec3.[33]
[g]Data obtained from European Commission report.[34]
[h]Estimated based on current market prices for XOS-derivatives.
[i]Price of electricity in Portugal.[35]
[j]Price of electricity in Chile.[36]
[k]Average price in Portugal.[37]
[l]Price estimated using correlations from literature.[38]

straight-line depreciation method was applied, where income tax of 21% (Portugal) and 27% (Chile), and interest rates of 2% (Portugal) and 2.75% (Chile) were assumed. Table 7 summarizes the economic data for raw material, products and utilities for both countries.

The economic viability of the small-scale biorefineries both in Portugal and Chile were evaluated based on the net present value (NPV). Following the six-tenths-factor rule (Eqn (1)), the influence of the process scale was also assessed.[23] This analysis helps to decide which range of processing capacity is the most adequate for positive profitability margins:

$$Cost\ A = Cost\ B \times \left(\frac{Capacity\ A}{Capacity\ B} \right)^{0.6} \tag{1}$$

Life-cycle assessment

For the life-cycle analysis (LCA), the functional unit is 1 t of lignocellulosic feedstock, which is assessed from cradle-to-gate using SimaPro software (v8.5.2), the Ecoinvent database (v3.4), and the ReCiPe Midpoint (H) method. Figure 2 shows the subsystems considered for the LCA , as well as the process inputs and outputs for both Portuguese and Chilean case studies.

Results and discussion

Process simulation

Mass and energy balances obtained from the Aspen Plus model are summarized in Table 8 for both Portuguese and Chilean case studies. In terms of mass balance, both case studies have similar results because the same process model was used, despite the differences in process scale and feedstock composition. Major differences can be observed in energy balance and utility usage (steam and electricity), and this is due to the different approaches used in the two systems. In the Portuguese case study, cogeneration was designed to produce HP steam rather than MP and LP, to fulfill the most expensive utility requirements, leading to higher electricity production during steam expansion to atmospheric pressure. On the other hand, cogeneration in the Chilean case study was designed to produce HP, MP, and LP pressure, to reduce the external consumption of all types of process steam, thus leading to a lower production of electricity. However, both case studies are self-sufficient in electricity and generate a surplus that is sold to the grid.

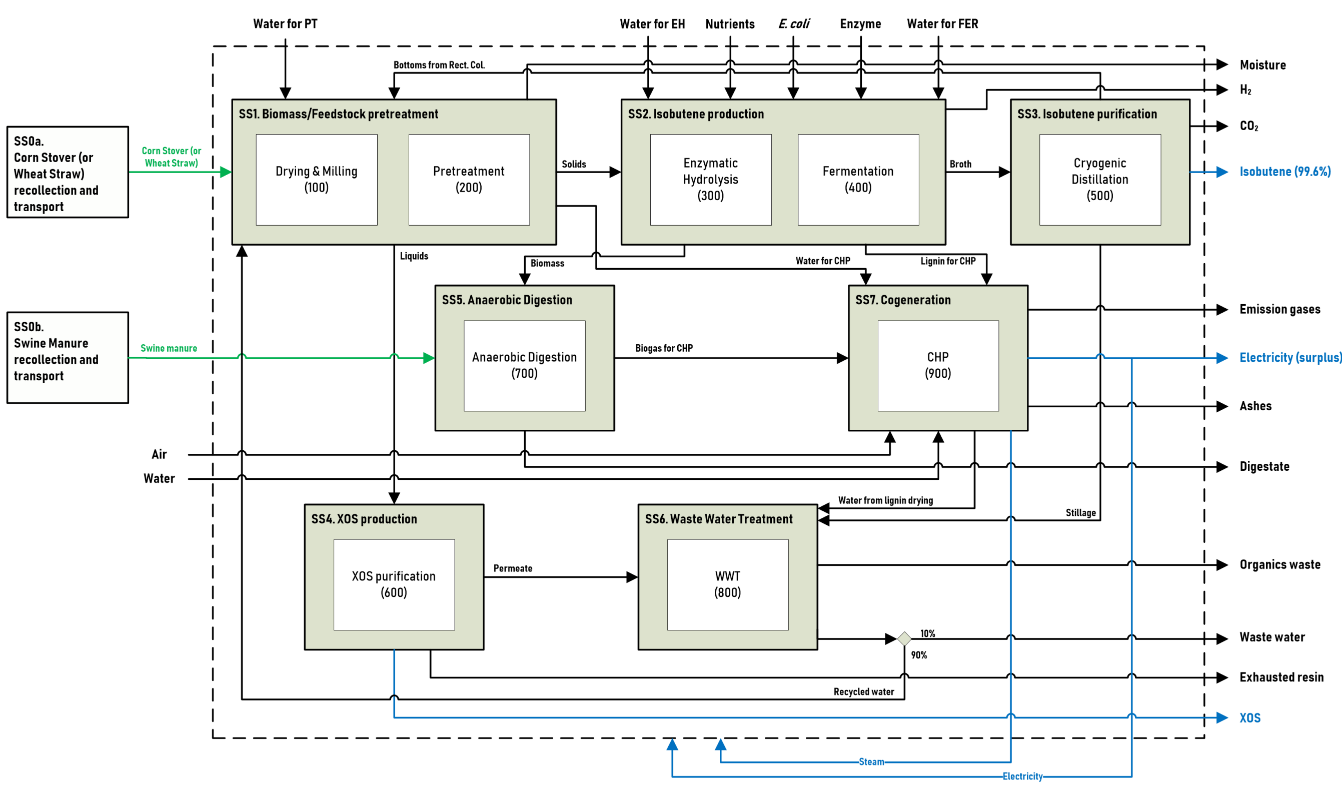

Figure 2. Process system boundaries for life cycle assessment (cradle to gate).

Table 8. Mass and energy balances obtained from Aspen Plus.

Inputs	kt per year	Outputs	kt per year	Utilities	kt per year
Portugal					
Corn stover	100.0	Isobutene (99.6%)	7.1	HP steam	2.8
Swine manure	46.5	XOS (85%)	8.4	MP steam	59.3
Nutrients	2.9	CO_2 from FERM	12.1	LP steam	0.0
E. coli	51.0	Emission gases	1511.1	Cooling water	1280.1
Enzymes	0.6	Ashes	2.9	Electricity (MW)	
		Organics waste	23.2	Process	28.83
				Surplus	18.80
Chile					
Wheat straw	32.0	Isobutene (99.6%)	2.7	HP steam	51.5
Swine manure	40.0	XOS (85%)	3.7	MP steam	28.1
Nutrients	0.7	CO_2 from FERM	4.7	LP steam	19.2
E. coli	8.2	Emission gases	158.0	Cooling water	541.1
Enzymes	0.1	Ashes	0.8	Electricity (MW)	
		Organics waste	14.6	Process	0.50
				Surplus	0.03

Table 9. Isobutene and XOS production costs from corn stover and wheat straw in Portugal and Chile, respectively.

Categories	Corn stover (Portugal)			Wheat straw (Chile)		
	Isobutene[a] (US$/t)	XOS[b] (US$/t)	Share (%)	Isobutene[a] (US$/t)	XOS[b] (US$/t)	Share (%)
Raw materials	249.1	295.4	25.0	88.2	120.8	7.7
Utilities	174.9	207.4	17.5	30.5	41.8	2.7
Maintenance	182.9	216.9	18.3	179.2	245.6	1.1
Labor	3.3	3.9	0.3	12.9	17.7	15.7
Fixed and general	111.9	132.7	11.2	73.51	100.74	6.5
Overhead	97.1	115.2	9.7	108.9	149.3	9.6
Capital depreciation[c]	178.3	211.5	17.9	645.5	884.58	56.7
Total cost	997.3	1182.9	—	1138.8	1560.58	—

[a]Production cost of isobutene = [(annual operating cost) ÷ (total annual production of isobutene+XOS)] × (mass fraction of isobutene).
[b]Production cost of XOS = [(annual operating cost) ÷ (total annual production of isobutene+XOS)] × (mass fraction of XOS).
[c]Calculated using the straight-line method.

Economic evaluation

Regarding the economic assessment, the production costs of isobutene and XOS from corn stover and wheat straw in Portugal and Chile, respectively, are summarized in Table 9. Due to the different locations chosen for each biorefinery, the economic parameters of both countries have a significant influence on total production costs and the shares associated with each category. In the Portuguese case study, the developed biorefinery for 100 000 tonne per year of corn stover leads to production costs of ca. 1 US$/kg of isobutene and 1.18 US$/kg of XOS, the raw materials cost being the highest contributor to the total cost. Whereas in the Chilean case study, the 32 000 tonne per year of wheat straw integrated biorefinery leads to production costs of ca. 1.14 US$/kg of isobutene and 1.56 US$/kg of XOS, capital depreciation being the highest contributor. In comparison with the market prices for both products (isobutene: 2.02 US$/kg; XOS: 4.05 US$/kg), the profit margin can be high, especially for XOS.

Regarding the fixed capital investment, the CAPEX for the Portuguese biorefinery is ca. 89.5 million US$, while for the Chilean case it is ca. 76.3 million US$. When comparing the CAPEX figures, although the Chilean production scale is lower than in Portugal, a relatively close fixed capital investment was obtained. Considering the investment per processed feedstock, the Portuguese biorefinery requires an investment of ca. 895 US$/t, whereas the Chilean biorefinery needs an investment of ca. 2384 US$/t. This is due to the different processing scales but also, mainly, to the high investment required in energy cogeneration systems, whose cost increased only slightly with a large increase in scale.

Figure 3 represents the variation in the NPV for both cases with the process scale. One can observe a similar trend in both case studies, with a slight difference that results in an economically viable process for any scale higher than ca. 40 000 tonne per year of corn stover (Portugal) and any scale higher than ca. 30 000 tonne per year of wheat straw (Chile).

These results are aligned with the isobutene production process claimed by Global Bioenergies because the use of cheaper feedstock (such as corn stover or wheat straw) for the production of isobutene, together with other high added-value co-products, can lead to the economic feasibility of an experimentally validated process.[24]

A sensitivity analysis was performed to evaluate the effect of the market price variation of raw material, utilities, and products on the economic feasibility of the process (data not shown). Briefly, the variation in the XOS market price is the parameter that has highest impact on the economic feasibility of the process. It is therefore important to ensure, technically, the recovery of XOS with high yield and purity to maximize the profit. Beside the market price of XOS, the variation of the cellulose content after pretreatment would affect the economic viability of the process because the decrease in the cellulose content would lead to a decrease in enzyme cost but also to lower sugar production – that is, lower profit.

Environmental impacts

The life-cycle inventory was obtained for the mass and energy balances and can be analyzed in detail in the supplementary data for both cases.

Regarding the climate change (CC) impact of the integrated biorefineries, the results are very similar for both cases. Corn stover / swine manure-based biorefinery (Portugal case study) has a total CC impact of 0.796 $kg_{CO2eq.}/kg_{corn\ stover}$ (economic allocation – isobutene: 0.193; XOS: 0.460; electricity: 0.143), while the Chilean biorefinery, wheat straw / swine manure-based, leads to a total CC impact of 0.760 $kg_{CO2eq.}/kg_{wheat\ straw}$ (economic allocation – isobutene: 0.185, XOS: 0.439, electricity: 0.136). Considering the isobutene yields and economic allocation, the CC impact is 2.72 $kg_{CO2eq.}/kg_{isobutene}$ (60.75 $kg_{CO2eq.}/GJ_{isobutene}$) and 2.19 $kg_{CO2eq.}/kg_{isobutene}$ (48.83 $kg_{CO2eq.}/GJ_{isobutene}$) in Portugal and Chile, respectively.

Due to the co-production of XOS, an energy-based allocation is not the best option and thus an evaluation of greenhouse gas (GHG) savings following the EU Renewable Energy Directive (RED) directive methodology has not been attempted.

Regarding the remaining environmental impact categories, ozone depletion, marine eutrophication, and particulate matter formation are lower for the Chilean biorefinery, while for terrestrial acidification, freshwater eutrophication, agricultural land occupation, water depletion, and fossil depletion, the biorefinery located in Portugal has less impact, despite its larger scale.

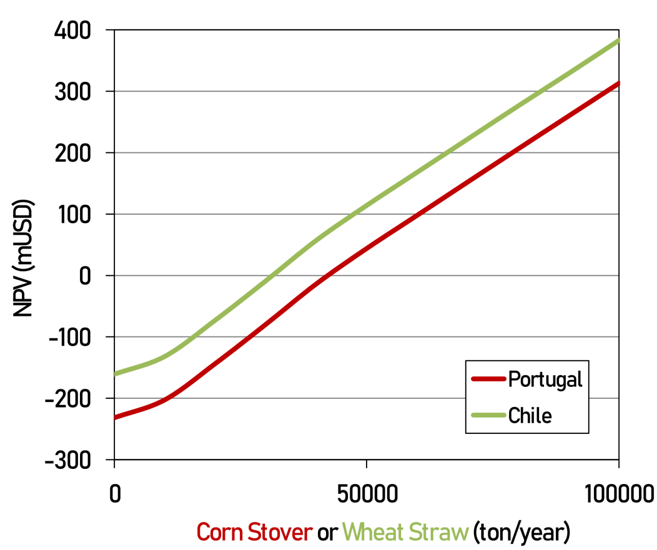

Figure 3. Variation of net present value (NPV) of the integrated biorefinery with the process scale, for both case studies.

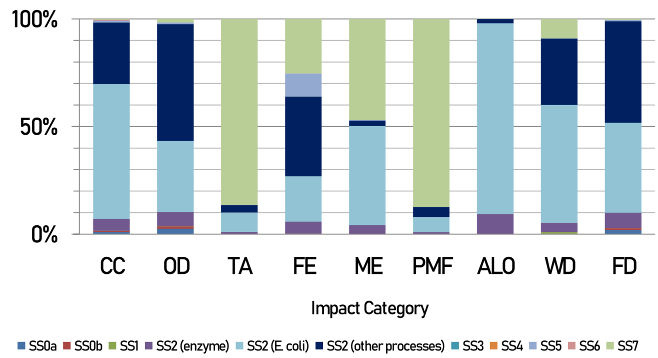

Figure 4. Environmental impact distribution per sub-system (SS) for Portuguese case study (Impact categories: CC – climate change, OD – ozone depletion, TA – terrestrial acidification, FE – freshwater eutrophication, ME – marine eutrophication, PMF – particulate matter formation, ALO – agricultural land occupation, WD – water depletion, FD – fossil depletion).

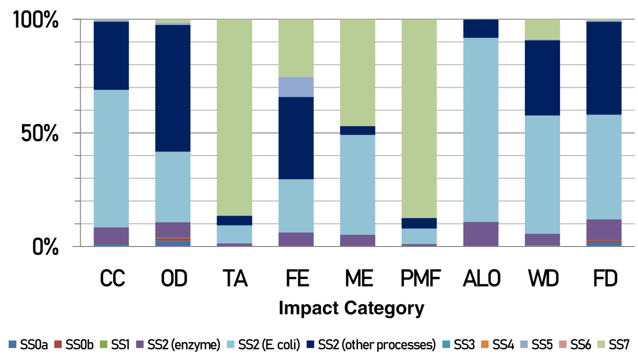

Figure 5. Environmental impact distribution per sub-system (SS) for Chilean case study (Impact categories: CC – climate change, OD – ozone depletion, TA – terrestrial acidification, FE – freshwater eutrophication, ME – marine eutrophication, PMF – particulate matter formation, ALO – agricultural land occupation, WD – water depletion, FD – fossil depletion).

Additional detailed information about all the environmental impact categories assessed can be found in the supplementary data.

The environmental impact distribution per subsystem is shown in Fig. 4 (Portugal) and Fig. 5 (Chile). The environmental performance of both cases (Portugal and Chile) is similar in each subsystem. Greater differences were obtained in SS2, due to the impacts associated with the transport of enzymes overseas to Chile, because the enzymes are produced in Europe. SS7 (CHP) has the highest impact on particulate matter formation (PMF), due to emission gases from the biomass burning in boilers.

However, as far as the authors are aware, no reports exist on the economic and environmental assessment of integrated biorefineries for producing isobutene from lignocellulosics. Most of the studies focused on ethanol production. The fermentative production of isobutene requires more research to reach large-scale production.[25] Most of the efforts have focused on developing metabolic engineering microorganisms.

Conclusions

Isobutene production in an integrated biorefinery using residues from cereal crops and swine manure is techno-economically viable in both Portugal and Chile.

The economic viability of such processes is related to the added-value byproduct obtained from both feedstock (XOS) and to the surplus electricity generated by burning both lignin and biogas. The economic parameters for each country have different effects on the OPEX and CAPEX of the process, leading to slight differences in their contribution to costs.

Regarding sustainability assessment, in a general way, the remaining environmental impact categories have similar results for both countries. However, for some impact categories, some significant differences are observed – for example, the biorefinery located in Chile has lower GHG emissions per kg of isobutene, although it has higher emissions per kg of feedstock, mainly due to the different composition of wheat straw and corn stover, which consequently leads to different isobutene yields.

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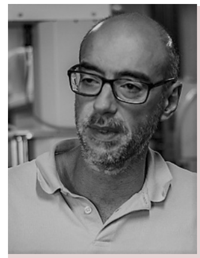
Tiago F. Lopes

Tiago F. Lopes has a PhD in refining, and petrochemical and chemical engineering. Currently, he is a researcher at the bioenergy unit of the Laboratório Nacional de Energia e Geologia (LNEG). His research interests include process modeling, techno-economic analysis and sustainability assessment of biorefineries.

Florbela Carvalheiro

Florbela Carvalheiro has a PhD in agro-industrial engineering from the University of Lisbon. Currently, she is a research scientist at the bioenergy unit of LNEG. Her research interests focus on the development of mild pre-treatments / fractionation processes aiming for the integrated upgrading of biomass.



Luís C. Duarte

Luís C. Duarte is a researcher at LNEG. He is interested in the experimental and modeling aspects of the development of integrated biomass upgrade processes within the biorefinery framework.

Francisco Gírio

Francisco Gírio is a principal researcher and head of the Bioenergy Department of LNEG. He is the SP3 Coordinator of European Energy Research Alliance (EERA)–Bioenergy and Vice-Chair of WG2–Conversion of European Technology and Innovation Platform (ETIP)–Bioenergy. His research interests include bioenergy and circular bioeconomy.

Julián A. Quintero

Julián A. Quintero has a PhD in engineering from the Universidad Nacional de Colombia. Currently, he is an assistant professor at the Universidad de Santiago de Chile. His research interests include biomass and agroindustrial waste valorization, biorefinery design, LCA, and process simulation.

Germán Aroca

Germán Aroca has a PhD in biochemical engineering. He is currently a full professor at the Pontifical Catholic University of Valparaíso in Chile. His research interests include production of 2G biofuels, biological treatment of gaseous emissions, modeling, simulation, and LCA of bioprocesses.