Techno-economic and environmental evaluation of lignocellulosic biochemical refineries: need for a modular platform for integrated assessment (MPIA)

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Ethanol production from lignocellulosic residues has potential to significantly improve sustainability of biofuels for transport by avoiding land-use competition with food crops and reducing impacts related to agricultural inputs. However, high production costs remain a bottleneck for large-scale development of this pathway. A huge potential exists in upgrading energy producing pathways into biorefineries in order to improve its economic performance and long-term sustainability. A promising general model for a lignocellulosic biorefinery is based on sugar-lignin platform, in which 5-carbon (C5) and 6-carbon (C6) sugars, resulting from lignocellulosic matrix fractionation, are converted into fuels and building block chemicals by biotechnological or chemical pathways. Boosting the development of lignocellulosic biochemical refineries (LCBR) is a complex and challenging task. First of all, capital and operation costs must be substantially reduced while minimizing environmental impacts from a life cycle perspective. Some strategies are envisioned as milestones leading to this end. The pre-treatment step must be optimized in order to improve the biomass accessibility to enzymatic and fermentative processes (alternatives include dilute acid pre-hydrolysis and hydrothermal methods). Advances in the development of recombinant micro-organisms capable of co-fermentation and able to survive in a broad range of reaction conditions can allow increased process integration with a significant reduction in capital investment. In this context, comprehensive, flexible and dynamic modelling approaches are needed to solve a problem with multiple optimization criteria (economic and environmental), high levels of uncertainty and dynamic behaviour. Process simulators and comprehensive databases of production processes can help to determine rigorous and thermodynamically consistent material and energy balances permitting robust scale-up and reducing uncertainty in economical and environmental impact evaluation in a dynamic context. This paper discusses the need for developing a modular platform for process synthesis aiming at selection of technically, economically and environmentally sound pathways for lignocellulosic biorefineries.

Keywords: Biofuels, Biorefineries, Optimisation, Process design

Introduction

Partial replacement of petrol by fuels produced from readily fermentable carbohydrates could only be seen as a transitional strategy, among many others, in order to phase-out fossil fuel consumption. Lignocellulosic biomass (LB) is increasingly being seen as both a sustainable and a low-cost feedstock for the production of fuels, energy and commodity chemicals, following the intense fractionation scheme of a petroleum refinery. LB [1] resulting from agro-industrial residues from corn, barley, oat, rice, wheat, sorghum and sugarcane could produce up to 442 Gl of bioethanol per year. A promising general model for a lignocellulosic biorefinery is based on sugar-lignin platform, in which 5-carbon (C5) and 6-carbon (C6) sugars, resulting from lignocellulosic matrix fractionation into its main components (hemicellulose, cellulose and lignin) are converted into fuels and building block chemicals by biotechnological or chemical pathways.

Cellulose is recalcitrant to biodegradation and needs to be hydrolysed in an initial pretreatment step into its constituent cellobiose units and into simpler *D.* glucose units in order to be liable to biochemical conversion. Hemicellulose components are rapidly solubilised and include polysaccharides such as xylan -composed of xylose units, a C5 sugar- and mannan -composed of mannose units, a C6 sugar-, intertwined with acetate groups that can be easily solubilised into acetic acid during pretreatment step. Ethanol production from LB can be considered as backbone of lignocellulosic biochemical refineries (LCBR) (Fig. 1). For first generation biofuels, feedstock represents a high share of production costs (near to 70%), which is not the case for second generation biofuels, in which the share decreases and becomes less than 40%[2, 3]. High production costs and technological uncertainties remain a bottleneck for large-scale development of this pathway that will increasingly depend on environmental and social concerns as well as on economic factors[2-4].

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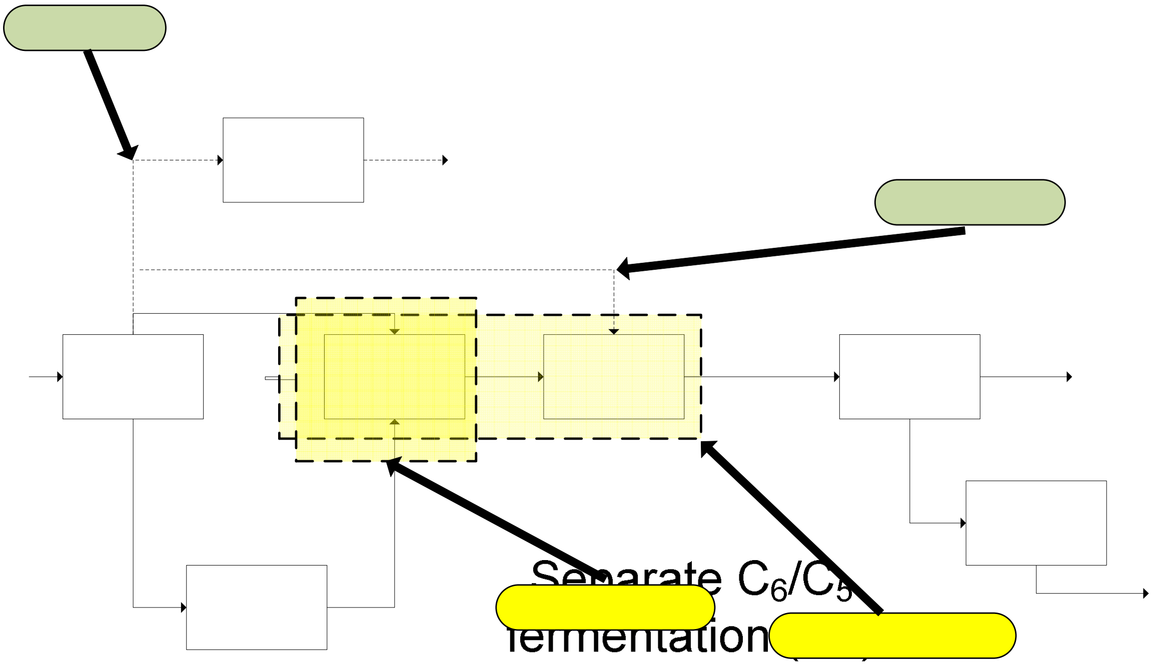

Fig. 1- Flowsheet with lignocellulosic ethanol production as the backbone of LCBR

Crucial steps (Table 1) are the pretreatment and the coupling of saccharification and fermentation stage[2,5]. Enzymatic hydrolysis approach shows a high potential for development due to recent progress in molecular biology. However, a preliminary fractionation step is still necessary. At the end of the last century, a significant cost reduction has been achieved for enzymatic hydrolysis [4].An ideal pretreatment step[6] should yield a hydrolysate with undegraded pentoses, reduced production of fermentation inhibitors and exhibiting a good suitability to work at high solid/liquid ratio. National Renewable Energy Laboratory (NREL) models[7,8], developed in close cooperation with highly experienced enzyme producers (Novozymes Biotech), include dilute acid as pretreatment, consider hardwood and agricultural residues as feedstock, show different levels of process integration and take advantage of fermentation organisms that must be tolerant to different operation temperatures and must be capable of using different substrates with high selectivity. This paper discusses developments at Swiss Federal Institute of Technology Lausanne (EPFL) of a Modular Platform for Integrated Assessment (MPIA) for LCBR including logistics optimisation, process design and simulation, process economics and life cycle assessment (LCA).

Table 1. Few technological non-exclusive options for different process stages of lignocellulosic biochemical processing into ethanol

Process stage	Technological variant
Pretreatment	AFE (Ammonia fiber explosion); Concentrated acid hydrolysis; Dilute acid hydrolysis; Alkaline hydrolysis; Milling; Steam explosion; Autohydrolysis
Cellulose hydrolysis and fermentation	Enzymatic cellulose hydrolysis with or without in-situ cellulase production (batch production, continuous solid state fermentation, cellulase recycling); Separate hydrolysis and fermentation (SHF); Simultaneous saccharification and glucose fermentation (SSF); Simultaneous sacharification and co-fermentation (SSCF)
Final products and co-products processing	Lignin utilization (Co-generation, pyrolysis, enzymatic depolymerisation); Xylitol production from pentoses; Polymerisation of lactic acid (if lactic acid is fermentation product); Ethanol separation (fractional distillation, selective sorption); Ethanol dehydration (Molecular sieve separation. pervaporation, azeotropic distillation); Vinasses treatment (co-generation, methanisation. composting, land-filling)

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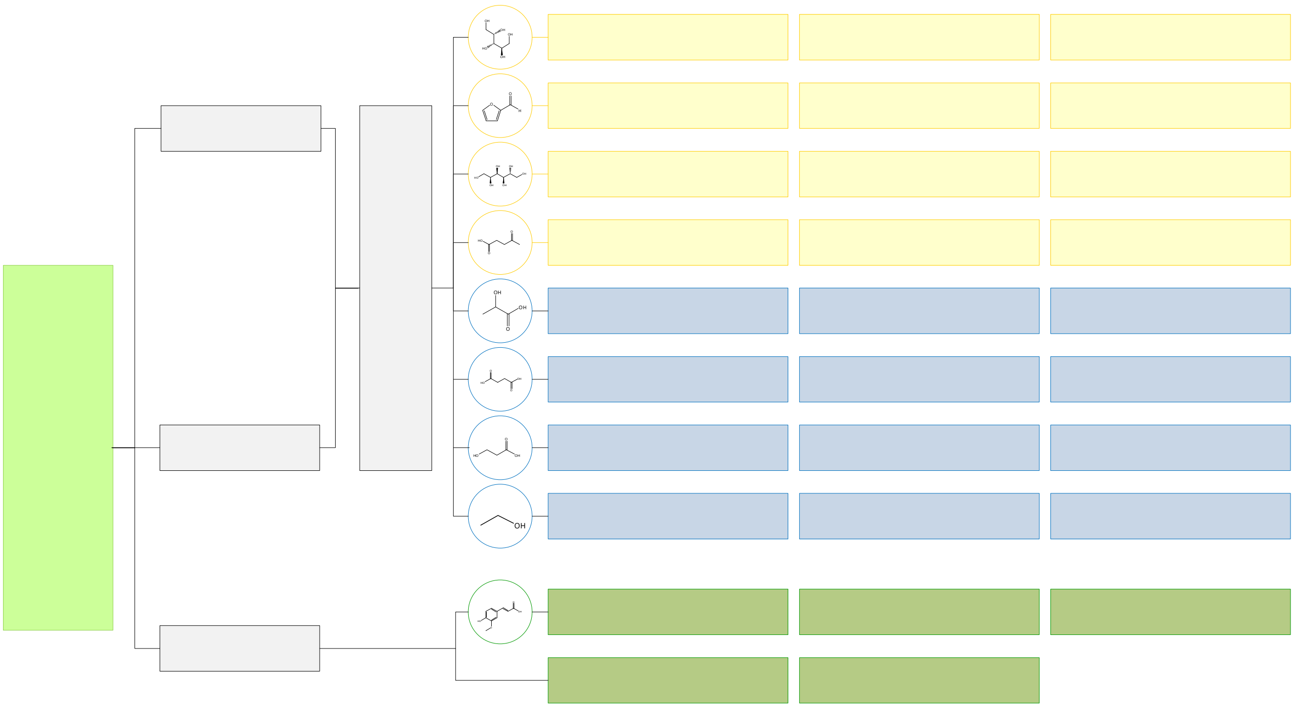

Fig 2.- Diversification panorama of LCBR pathways

Modelling Biochemical Pathways for Biorefineries and Lignocellulosic Ethanol Production: State-of- Art

Upgrading and Diversification

A huge potential exists in upgrading fuel and energy producing pathways into biorefineries in order to improve their economic performance and long-term sustainability (Fig 2). In LCBR process, biomass conversion leads to a multifunctional system producing fuels, value added chemicals and possibly power generation.

There are multiple potentialities for a lignocellulosic or second generation biorefinery in which biomass is fractionated after a pre-treatment step into cellulose, hemicellulose and lignin. Cellulose could be hydrolysed into glucose and then fermented into ethanol or another bioproducts such as lactic acid, building block for polylactides that are potential substitutes for polyethylene, an important fossil derived chemical commodity. Soluble hemicellulose could also be fermented into ethanol or other co-products as xylitol, used as sweetener; in addition, products resulting from detoxification of hemicellulose hydrolysate, such as furan derivatives and phenolic compounds, could be used as building blocks for the production of fibers and resins. Lignin can be burned to produce steam or power, pyrolysed, or enzymatically depolymerised to produce mono-aromatic compounds such as gallic and ferulic acids, building blocks for phenolic resins and fibers. Biorefinery concept offers an enormous potential for valorisation and long-term sustainability of biofuels production [4,9-13]. Santos *et al*[14] described the experience of producing xylitol from sugarcane bagasse fibers. Gonçalves & Benar[15] also reported the hydroxymethylation and oxidation of organosolv lignins.

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Supply-side Module

Supply logistics for bioenergy systems has been studied under a GIS based framework[16-18]. Production cost of ethanol from LB is quite sensitive to economy of scale[7,8,19]. On the other hand, for processes dealing with high volumes of raw material and high capital costs, marginal changes in feedstock cost can make the difference[16,17]. Therefore, in assessing the economic viability of a LCBR, trade-off between plant size and raw material *delivered cost* must be taken into account. Estimation of feedstock cost is not straightforward due to the lack of formal markets for a large part of LB and due to site-specific availability and procurement constraints. Delivered costs can be calculated as the sum of *farm gate costs* (costs incurred in feedstock handling at farm) and *transport-related* costs (loading and unloading cost, costs due to transportation from farm to the plant gate, and administrative costs) [17]. The farm gate price may vary from one farm type to the other, depending on the farm size and on the agricultural practices (e.g. more or less mechanisation, competition between uses, competitions between farms, income of farmers), and therefore has a strong spatial variability [18]. The NREL, [8, 20] estimated the farm gate price of corn stover for ethanol production by adding costs of fertilizer inputs (17 %), baling and staging (60%) and a premium given to farmers (23%), calculated as a fixed profit per area unit representing the likely threshold above which farmers would accept the risk and added work of collecting and selling their residue. On the other hand, transport costs are directly related to plant size. In the NREL study, transport costs represented 23% of total delivered cost, for a plant processing 2000 tons per day. Some researchers [16, 17] linked the bulky nature of LB with a significant impact in transportations costs underlining the importance of plant location and plant size. A GIS-based methodology[17] to determine marginal price surfaces under several facility size scenarios was applied to potential switchgrass-to ethanol conversion facilities in Alabama (US). Using GIS, NREL and Oak Ridge National Laboratory (ORNL, US) developed a model to estimate energy and environmental flows and costs for collection and transportation of corn stover in the state of Iowa, accounting for soil erosion constraints[8,21]. For this model, sustainable corn stover removal rate was estimated to 5 tons/ha for no-till practice and no crop rotation. It was estimated that 10 % of total farm area would correspond to these characteristics. EPFL[18] developed a GIS-based decision support system (DSS) for selecting least-cost bioenergy locations when there is a significant variability in biomass farm gate prices and when several bioenergy plants with a fixed capacity have to be placed in the region. Valorisation of agricultural residues represents an alternative to open-field burning strategies, which are increasingly discouraged due to air pollution and soil depletion. Crop residues (sugarcane harvesting residues [22,23,24] and rice straw [1,25]) are burned as a low-cost strategy to facilitate harvesting and avoid plant diseases if residues are left in the field. Softwood forest residues must also be correctly handled to improve forest health and reduce fire risks by using them as feedstock for ethanol production[7,26]. Kim & Dale[1] estimated potential for bioethanol production (205 Gl) from rice straw (731 Tg) per year, and also estimated potential of ethanol production (51.3 Gl) from bagasse, potential that can significantly increase if sugar cane harvesting residues are also used.

Process Design Aspects

Process design is the core of an integrated assessment for LBCR (Fig. 3) and, in particular, a basic input for supply logistics and process economics evaluation as well as for environmental impact assessment. Process simulators can provide rigorous material and energy balance calculations, which are thermodynamically consistent. The NREL[27] has developed an Aspen Plus (Aspen Technology Inc., USA) in-house database with thermodynamic and other physical properties specifically related to biomass for bioethanol production. Rigorous material and energy balances permit to evaluate technological options, represented by a particular flowsheet design, and obtain robust outputs regarding environmental impacts and economic viability, with a level of detail related to the stage of bioenergy project and Feedstock supply and composition are important issues that influence the choice of flowsheet design and overall pathway performance[7]. In particular, feedstock composition (Table 2) may determine the choice of the pre-treatment strategy and other downstream process choices. Hardwoods are, in general less recalcitrant to pretreatment than softwoods, because their hemicelluloses are

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composed of highly acetylated xylans and acetate groups that rapidly hydrolyses into acetic acid in water, encouraging autohydrolysis of sugar polymers. In that sense, hardwoods are more susceptible than softwoods to autohydrolysis-low-severity methods[29,30]. Hardwoods also present lower contents of readily fermentable sugars (C6), as do agricultural residues and herbaceous crops. This implies: 1) Selection of a pretreatment method that encourages hemicellulose recovery while maintaining acceptable rates of cellulose hydrolysis and low levels of soluble inhibitors; and 2) Selection of downstream strategies aimed at valorisation of C5 and C6 sugars. Thus, one could obtain valuable information on process design trade-offs if process simulator dynamically responds to changes in inflow rate and feedstock compositions taking appropriate flowsheeting choices, while maintaining thermodynamic and individual equipment sizing consistency. Kinetic models predicting conversions can be of great help to support dynamics and semi-automation of process simulation depending on feedstock characteristics and operational conditions.

Pretreatment Kinetics

A common approach to tackle pretreatment kinetics consists of using a parameter relating reaction conditions into a single reaction ordinate to facilitate comparisons between different pretreatment methods and to use it in predictive models of sugar recovery and yield of enzymatic hydrolysis[30,31]. The severity factor, R_0, for biomass pre-treatment was first proposed by Overend and Chornet [32] as a trade-off between reaction temperature and residence time in an approximation to the Arrhenius equation. Bouchard *et al*[33] related R_0 to evolution of water soluble hemicellulosic fractions (pentosans and acetyl groups), and of compounds derived from lignin (methoxyl groups and polyphenolics).

$$R_0 = t * e^{(T_r - T_b / \omega)} \quad \ldots(1)$$

$$\omega = \frac{T_f^2 R}{E_a} \quad \ldots(2)$$

where, t= time (min), Tr= reaction temperature, Tb= base temperature, usually set to 100°C, ω = constant, Tf= Floor temperature, R=Universal gas constant, and Ea=Activation energy

To better fit for experimental data of acid catalysed steam pretreatment or organosolv pretreatment, Chum *et al*[34] proposed combined severity factor (CS), which also assumes a first order rate contribution from acid catalyst. Tengborg *et al*[29] used the combined severity factor to describe pretreatment of softwood with different degrees of H_2SO_4 impregnation in production of ethanol at different reaction conditions and related this parameter to yields of fermentable sugars and ethanol.

$$CS = \log(R_0) - pH \quad \ldots(3)$$

where, pH= pH at reaction conditions

Hemicellulose solubilisation kinetics has been the focus of various studies for dilute acid pretreatment [35] and for autohydrolysis pretreatments[36-38]. In general, this kind of model is based on assumptions such as pseudo-homogeneous conditions, first order kinetics and Arrhenius-type dependence of temperature. In fact, initial solid concentrations are important to determine reactor volume and design. Therefore, homogeneous kinetics could not exactly represent variations from batch to continuous reactors. Jacobsen & Wyman[36] the contested adequacy of batch-test based-homogeneous-first order kinetic models, which assume direct conversion of hemicellulose into sugar monomers. Cannetieri *et al*[35], though used pseudo-homogeneous kinetics to model dilute acid hydrolysis of forest residues for simplicity reasons, recognised that heterogeneous models are a better representation of real conditions and found consistent kinetic constants following Arrhenius theory describing hemicellulose degradation into monomeric sugars and degradation products such as acetic acid, furfural and 5-hydroxymethyl furfural (from C6 sugars). Oligomeric intermediates become important in biorefinery developments that envision valorisation of oligosaccharides in food and pharmaceutical industries[37,38]. Nabarlatz *et al*[37] developed and validated a model for kinetics of xylan autohydrolysis with experimental results from pretreated corncobs. Carvalheiro *et al*[38] tested different sequential pseudo-homogeneous first-order kinetic models for brewery's spent grain autohydrolyis taking into account hydrolysis of xylan and arabinan and xylose dehydration to furfural.

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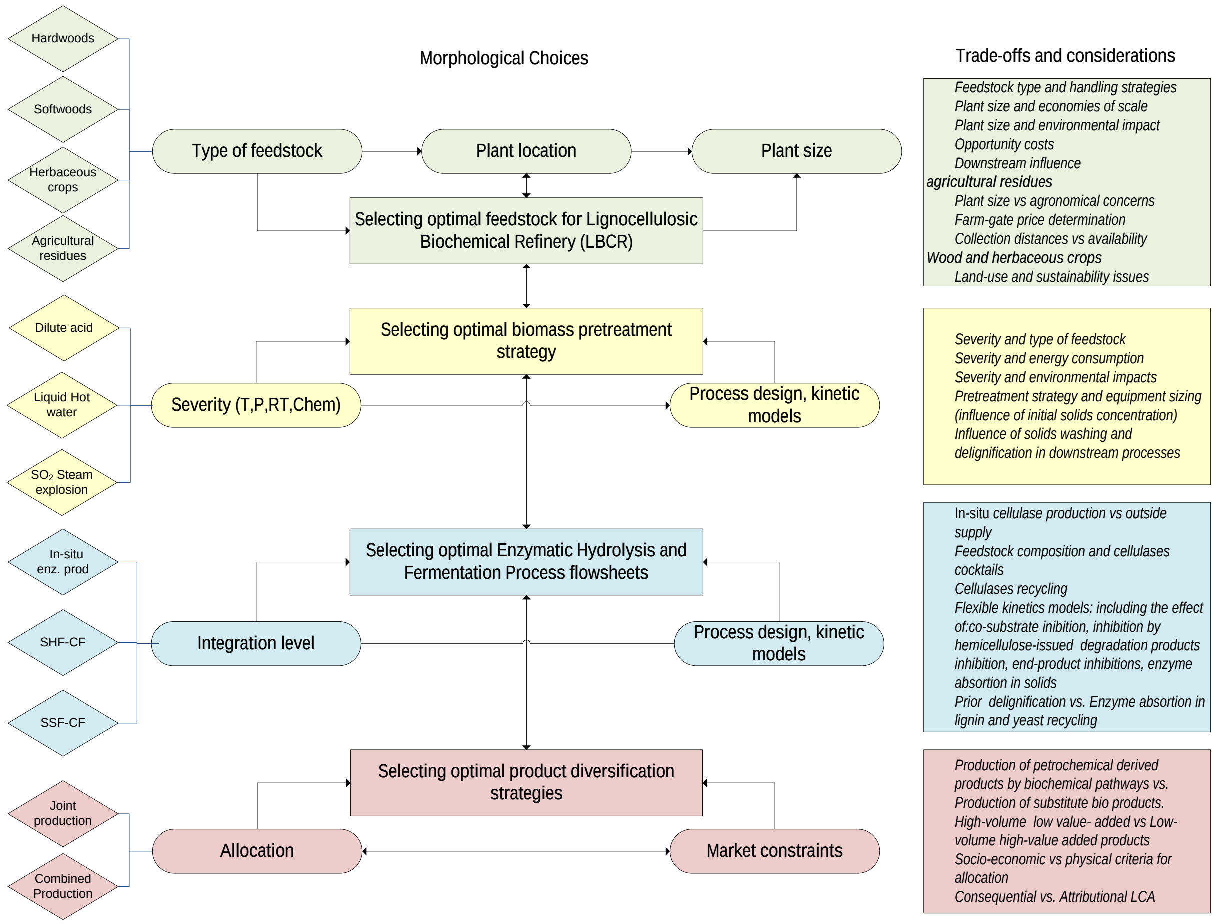

Fig.3 – Potential trade-offs related to supply logistics and process design

Table 2. Usual composition of common type of feedstock

Feedstock	Hardwood (yellow poplar)[7]	Softwood (pine)[28]	Herbaceous crops (switchgrass) [28]	Agricultural residues (corn stover) [8]
Cellulose (Glucan C6)	**42.4**	**44.55**	**31.98**	**37.4**
Hemicellulose	**21.5**	**21.89**	**25.18**	**27.6**
Xylan C5	18.1	6.3	21.09	21.1
Arabinan C5	0.5	1.6	2.84	2.9
Mannan C6	2.9	11.43	0.3	1.6
Galactan C6	0	2.56	0.95	2
Acetate	**4.6**	**2.67**	**1.21**	**2.9**
Lignin	**26.6**	**27.67**	**18.13**	**18**
Ash	**1**	**0.32**	**5.95**	**5.2**
Other	**3.9**	**2.88**	**17.54**	**8.9**

Saccharification and Fermentation Kinetics

According to South *et al.* [39], a kinetic model for simultaneous saccharification and fermentation (SSF) should predict substrate conversion, with reasonable accuracy over a significant range of initial substrate concentration, cellulase loadings and reaction time. Kadam *et al*[40] developed a kinetic model for enzymatic saccharification, based on corn stover saccharification but intended to be used in a general way for *in silico* process optimisation. The model consisted of three hydrolysis reactions (2 heterogeneous reactions for cellulose breakdown to cellobiose and glucose and 1 homogeneous reaction for hydrolysing cellobiose to glucose).The heterogeneous kinetic model took into account biochemistry of enzymatic hydrolysis, absorption and desorption phenomena for cellulose and lignin substrates, substrate reactivity, thermal effects and end-product inhibition. This model was based on previous modelling efforts, notably on the model developed by South *et al.* [39] intended to describe SSF in batch and continuous reactors and takes into account, additionally, fermentation by *Saccharomyces cerevisae* and ethanol inhibition.

All of these models follow Michaelis-Menten type of kinetics for hydrolysis of soluble cellobiose to glucose, use Langmuir competitive absorption models for heterogeneous cellulose-lignin system; and use pseudo first-order constants fitted with Monod kinetics for glucose and/or pentose fermentation and Arrhenius model for temperature dependence. Regarding the specific case of co-fermentation, Leksawasdi *et al*[41] presented a model for glucose and xylose fermentation taking into account substrate limitation, substrate inhibition and product (ethanol) inhibition.

Another aspect of great importance regarding the viability of cellulose hydrolysis processes is enzyme cost. Cellulase production represents an important share of ethanol production costs[7,8]. In the 1999 NREL's model of hardwood-to-ethanol pathway[7], *in-situ* cellulase production by submerged fermentation (SmF) from aerobic fungus *Trichoderma reesei* was envisioned. In the 2002 corn-stover-to-ethanol's model[8], cellulase off-site production was considered due to cost considerations. Installed capital operating costs associated to *in-situ* production were about US$0.079 per liter ethanol, whereas a cost of US$0.026 per liter of ethanol was estimated for enzyme delivered to the plant from a local enzyme facility. However, solid-state fermentation could imply lower energy requirements and lesser wastewater generation[42], becoming an interesting alternative to reduce costs of *in-situ* production. Coupling of kinetics models with process simulation can be a useful tool to improve economics and sustainability of bioconversion processes. For SmF processes, microorganism growth is often modeled following variants of Monod kinetics and enzyme production with variants of Leudeking piret model[43,44]. On the other hand, when developing solid-state kinetics, difficulty lies in separation of microbial biomass and substrate and therefore classical method for biomass growth determination are not suitable making necessary an adequate correlation with factors such as CO_2 production and O_2 consumption[44]. Using these control variables, a few attempts have been made to model kinetics of oxygen consumption and temperature dependence of solid-state fermentation systems in general[44-46].

Another way for enzyme-related costs reduction is an adequate recycling scheme of cellulases for the enzymatic hydrolysis stage. A kinetic model for enzymatic hydrolysis must take into account the competition for cellulase absorption between lignin and cellulose[39,40,47]. This competition can be a bottleneck for cellulase recycling if no previous delignification step is implemented. Addition of surfactants can be useful to decrease non-productive binding of cellulases to lignin[47].

Process design of upgrading alternatives of bioconversion of lignocellulosics processes into biorefineries can also be enhanced by adequate kinetics models. For example, lactic acid, an alternative to ethanol as a fermentation product, is a building block for polylactates, biodegradable polymers representing a potential substitute for polyethylene sharing with it similar physical properties such strength and elongation to break[4,48-50]. Luo *et al*[48] pointed out that using SSF for lactic acid production will take advantage of the fact that enzymatic hydrolysis and lactic acid fermentation work at similar optimal conditions of temperature and pH for a theoretical yield of 100% of lactic acid.. Kinetic models for cellulose symbiotic breakdown and for glucose consumption were developed taking into account competitive absorption with lignin. Xylitol is another potential biorefinery's output resulting from C5 hemicellulose which is mostly produced from chemical pathways but could be alternatively produced via fermentation of xyloses[51-53]. In addition to its use as a sweetener with anticariogenic properties, can also be used as plasticizer for hardwood xylans[52,54]. Rivas *et al*[52] estimated kinetic parameters and developed carbon material and bioenergetic balances for xylitol production from corncobs using yeasts.

Environmental Impact

LCA has been used for environmental impact evaluation of lignocellulosic ethanol production and can be a useful tool to evaluate LBCR in general[21,55-61]. LCA for biorefineries have been restricted mainly to diversification schemes of existing first generation food crops-to-biofuels pathways (wet mill cereal-to-ethanol pathway[58,62-64] or soybean oil valorisation chain[65]). Environmental impacts of LCBRs have only been estimated for pathways with a low degree of product diversification delivering ethanol and energy from lignin-rich residues[21,55,56,59-61]. However, there is a huge potential for large-scale production of bulk chemicals from dedicated lignocellulosic crops or agricultural residues to directly replace or at least to offer similar functions than its fossil-based counterparts. Presently, LCAs for highly diversified biorefineries must be restrained to generic approaches due to limitations in process data availability and uncertainty in technological developments. Hermann *et al*[66] performed LCA for an extended group of bio-chemicals assuming that the yield for sugar-based bioprocesses was independent of the type of sugar and therefore from the type of feedstock, recognising, however, the questionable adequacy of this simplification. In general, when evaluating the environmental performance of a LBCR by means of a LCA, there are some methodological issues, inherent to methodology which still generate a great deal of discussion and controversy between practitioners and policy makers. One of these issues, and also a main weakness of a LCA of a multi-product system, is the problem of allocation or the way in which environmental burdens are distributed between the multiple outputs of the biorefinery. The complexity of the allocation problem increases in the case of a highly diversified biorefinery -one producing various commodity chemicals and energy. Presently, most of the products envisioned for a LBCR have no formal or established markets[4,67]. In occasions, these new products are substitutes for petrochemical commodities providing also additional or slightly different functions, hampering by this fact the application of economic or substitution approaches. Multi-functionality could also make difficult an appropriate value attribution to perform an allocation based on physical properties such as energy content, mass or carbon contents. In addition, a system of this kind will probably present a highly dynamic nature due to supply-demand evolution linked to changes in production priorities and investment strategies. In that sense, consequential variants to conventional LCA methodology can be an option to deal with this issue. A consequential LCA can be defined, in contrast to an attributional LCA, as a methodology aimed at the description of how environmentally relevant physical flows to and from technosphere will change in response to possible changes in the life cycle including unit processes that are significantly affected whether they are inside or outside the life cycle[68]. A LCA framework coupled with partial equilibrium microeconomic models, as that used by Freire *et al*[69] to optimise resource allocation and policy scenarios for biofuel introduction in France, offers possibilities to be extended to the dynamic behaviour assessment of biorefineries.

Another weakness of LCA is related to linearity that governs input/output relations in that method. Non-linearity of production functions, particularly in the case of highly diversified biorefinery processes, is common rule. Mathematical relationships describing a process are, in general, dynamic and non-linear and this may be taken into account in LCA practice depending on assessment objectives, data and dedicated software availability and accuracy and robustness constraints[70]. In that sense, process simulators can help to evaluate to which extent the assumption of linearity for a particular production function is consistent with reality. Moreover, coupling of rigorous process design and LCA has been proposed to optimise production process according to environmental and economic criteria[71-74]. Since 1970's oil crisis, objectives in process design have shifted, first to incorporate energy savings into chemical process and then to increasingly include environmental and sustainability concerns. Cano Ruiz & McRae[71] reviewed methodological issues and research needs

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related to integration of environmental concerns including LCA as a framework to estimate environmental impacts as well as, for process synthesis, hierarchical design approaches, expert systems and other artificial intelligence approaches. Azapagic[72] recommended inclusion of LCA in the first stages of process design using a mixed integer linear programming (MILP) multi-objective optimisation in order to identify a set of Pareto-optimum solutions for improved design. Chen *et al*[73] presented results of a multi-objective optimisation of a volatile organic chemicals (VOC) recovery process and a heat exchanger network (HEN), coupling process simulation using HYSYS (Aspen Technology Inc., USA) with LCA. Environmental Fate and Risk assessment Tool (EFRAT) was used for impact assessment and annualised capital and operating costs were used as economic performance indicators. Optimisation was carried out through Analytical Hierarchy Process (AHP). Quintero *et al*[75] followed a similar approach and applied it to first generation ethanol production pathways. Most of the emphasis in multi-objective optimisation approaches using LCA has been put in process design aspects. However, supply logistic plays an important role in an integrated assessment of LCBR and in bioprocesses in general. Hugo & Pistikopoulos[74] developed a MILP combining classical plant location and capacity expansion problem with the concepts of LCA and multi-enterprise supply chain management. They used Eco-indicator 99 as aggregation factor for impact assessment and conventional net present value (NPV) as economic performance measure of vinyl chloride monomer (VCM) and ethylene glycol (EG) supply chain. Complexity of overall problem requires effective optimization algorithms in order to reduce computational burdens and assure convergence. Steffens *et al.* [76] illustrated potentialities for application in bioprocesses of *Jacaranda* system, a Java written application, useful for multicriteria process synthesis. This application uses discretisation to convert a mixed integer non-linear programming into a graph generation and search problem. The algorithm proved able to generate a list of N-best flowsheets in a reasonable computational time for a penicillin production process restricted to the manufacturing stage. While *et al*[77] developed a multi-objective evolutionary algorithm for mineral processing optimisation and process design. Jan *et al*[78] developed a new hybrid Genetic/Quadratic search algorithm (GQSA), coded in MATLAB® Version 6.0, to optimise plant economics when a process simulator models the plant. They took advantage of Active X components in Aspen Plus (Aspen Technology Inc., USA).

Process Economics

Economic viability of lignocellulosic-based bioprocesses has been studied through detailed process design data in order to optimise research direction[7,8,79-82]. Nguyen & Saddler[79] developed a process simulation model using Lotus 123 (IBM, USA) to evaluate the technical and economic feasibility of a plant processing 500 tons of aspen wood per day to produce ethanol, using SO_2 catalysed steam explosion, delignification and separate pentoses fermentation. Feedstock, enzyme production, efficiency of cellulose hydrolysis, ethanol yield from xyloses, efficiency of delignification and credit attributed to lignin as fuel co-product were major contributors to production cost of ethanol from wood. NREL models from 1999[7] and 2002[8] established process design models and cost estimates for hardwood-to-ethanol and corn stover-to-ethanol pathways, respectively. Aspen Plus (Aspen Technology Inc., USA) process simulator was used to estimate material and energy balances. Capital costs and equipment sizing were evaluated through vendor quotes and estimations from ICARUS Process Evaluator (Aspen Technology Inc., USA). In the 2002 version, NREL changed the base case feedstock from yellow poplar to corn stover which was considered as a promising feedstock, and left behind SSF as well as *in-situ* enzyme production in order to better portray the state of research. For this pathway, they calculated the minimum selling price (MESP) of ethanol in US$0.283 per liter using a Discounted Cash Flow (DCF) model and Montecarlo simulation. Using a similar approach, other researchers[81,83] studied trade-offs for softwood-to-ethanol pathway, including the effect of enzyme costs on ethanol production total costs, substrate loading in SSF and SHF modes, and various schemes of stream recirculation and steam pre-treatment configurations. In a previous work at the EPFL[80], different alternatives of sweet sorghum valorisation, including among others co-generation and ethanol production from sweet sorghum bagasse, were compared through process simulation with Aspen

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Plus and economic performance analysis. In the framework of the Biomass Refining Consortium for Applied Fundamentals (CAFI) UDA Initiative for Future Agriculture and Food Systems (IFAFS)[82], techno-economic models for five biomass pretreatments (dilute acid, hot water, AFEX, ammonia recycle percolation (ARP) and lime) were developed and inserted into 2002 NREL model. In general, all of these studies use process simulation and DCF models to assess different technological variants. None of these variants include a diversification strategy to produce bulk chemicals from sugars or a different alternative to fuel use for the lignin-rich residue.

Until now, all techno-economic evaluations of lignocellulosics bioconversion processes have used DCF models, which rely on economic performance measures such as NPV, Internal Rate of return (IRR) and Discounted Payback Period (DPP). All of them can be used to compare alternative investments or projects of energy efficiency and renewable energy technologies[84]. However, NPV has been traditionally viewed as a more reliable measure of economic performance than the IRR and the DPP[85,86]. When using IRR certain cash flows can generate NPV=0 at two different discount rates, or can show NPV of a project increasing as discount rate increases, contrary to normal relationship between NPV and discount rates[85]. DPP presents also inconveniences such as the fact that it only accepts projects that payback in desired time frame ignoring later year cash flows and present value of these future cash flows[85]. However, traditional NPV analysis can also lead to underestimations of benefits associated with a project due to the implicit assumption that companies holds its assets passively, ignoring management flexibility and the intangible advantages linked to discretionary investment opportunities[85-87]. A biorefinery can be by nature a highly dynamic investment project. Biorefineries are multi-output systems characterised by implicit technological and market uncertainties, in which production priorities and investment decisions will be possibly much diversified across time. It is the case of lignocellulosics-to-ethanol production pathways, which are expected to be gradually upgraded into bulk-chemicals-and-fuels production pathways. For example, the production process of a specific biorefinery product, such as, lets say, biodegradable polylactates, can be presently too costly but offers instead a great potentiality to replace a fossil-based product of widely industrial use and even offers additional functions. In the years to come, substantial cost reductions could be attained for this pathway regarding control of fermentation inhibition, lactic acid recovery from fermentation broth and control of molecular weight and properties of final polymers [4, 53, 88]. Switching of dedicated crops to agricultural or even industrial residues also represents an investment opportunity that could add value to the project. To overcome limitations of conventional NPV when assessing the merit of a project like that of a biorefinery, some methodologies are proposed such as adjusted present value[86], which includes the impact of dynamic decision making and the value of real options. The real options for an investment project can be classified into six categories based upon the type of flexibility provided [86]: 1) option to defer (option to put off a decision until some date in the future provided further information is gathered); 2) option for staged investments (the project is broken into discrete phases and the next phase is not started until the current phase has been completed); 3) Option to change scale (the project can be expanded , contracted or shut down and restarted depending on market conditions); 4) option to abandon (also related to market conditions); 5) option to switch (option to change either the input or the output of the project, can be related to change in feedstock and/or biorefineries diversification); 6) option to grow (option to make investments based on future growth value even if there is a negative traditional net present value, related to the uncertainty in technological and market development of certain biorefinery products). In the IFAFS project [82], little differentiation was found between economic performances of biomass pretreatment strategies varying from low cost to capital intensive options. However, the study recognised that it was not completely fair to make economic comparisons between pretreatment options given the different stage of development between them. The study recommended using real options analysis to adjust DFC to differences in state of development, complexity, reliability, differing potential for creating environmental and safety uses, etc.

Even if real options are not considered, opportunity costs and competing uses of biomass

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must be taken into account when determining the economic performance of a LCBR. In the framework of biomass conversion, opportunity costs can be defined as the costs forgone by choosing one option of biomass valorisation over an alternative one that may be equally desired. In the already mentioned EPFL study [80], in which alternative uses were considered, including ethanol production for sorghum juice and sorghum bagasse, an opportunity cost approach was coupled to DCF models. A great sensitivity to ethanol and sugar prices was found, which resulted in the necessity of flexible installations capable of switching of production objective according to demand.

Alternative use of biomass was also evaluated for excess sugar cane bagasse utilisation [89]. In that interesting study, an approach considering competing onsite electricity production and offsite ethanol production was envisioned according not only to economic but to environmental objectives. The proposed model was called "Environmental System Optimization" under a LCA framework and using weighting factors for economic and environmental objectives. Instead of using process simulation inputs, their model relied on literature values and on SimaPro V5.1 (Pré Consultants, the Netherlands) which uses built-in Ecoinvent (Swiss Centre for Life Cycle Inventories, Switzerland) databases. After determining environmental impacts of the two options, they concluded that it was desirable utilising excess bagasse as feedstock for ethanol production, when environmental and economic aspects were concerned.

Modular Platform for Integrated Assessment (MPIA) of LCBRs

The Modular Platform for Integrated Assessment (MPIA) is proposed as a comprehensive option to evaluate LCBRs from an environmental and techno-economic point of view. The Platform would include 4 modules (logistics optimisation, process design and simulation, process economics and LCA) (Fig. 4). Modules presented here are deeply interconnected. Some of the modules will be partially automated in order to assess composition and scale issues. The platform will provide a DSS for designing and evaluation consistent LBCRs following a holistic approach. Ongoing research at EPFL is aimed at the development of multi-criteria optimisation approaches including evolutionary algorithms, hierarchical design approaches and other methods of structured thinking, expert systems and artificial intelligence approaches.

Supply-side Module

EPFL GIS-based DSS for selecting least-cost bioenergy locations is currently being expanded to the specific case of lignocellulosic bioethanol plants including an environmental objective function. This module aims at the estimation of the biomass potential to satisfy a given bioethanol demand based on political, social, economical, environmental, technological, and agro-ecological constraints and at determining optimal plant size and logistic configurations in order to reduce operational costs and environmental burdens. Information provided by this module is intended to be used along with LCA and automated process simulation tools.

Process Design Module

This module is based in the automation of Aspen Plus process simulator to investigate effects of plant size and feedstock type and composition throughout the whole life cycle of LCBR. Automation strategies are currently being developed at the EPFL by means of external automation software such as MATLAB and Visual Basic for applications (Microsoft Corp, USA) taking advantage of Active X components in Aspen Plus. These strategies include the development of user customised reactor units in Aspen Plus incorporating kinetic models for pretreatment, saccharification and fermentation steps. Kinetic models are intended, when possible, to take into account heterogeneity, substrate limitation, end-product inhibition, as well as inhibition from organic compounds resulting from biomass pretreatment.

Selection of pretreatment methods and configurations will depend on feedstock type and downstream integration and diversification choices, using C5 and C6 sugar yields after pretreatment as parameters.

The platform is being developed through lignocellulosic-to-ethanol pathways but will be extended to more diversified pathways after validation and tuning with these backbone pathways.

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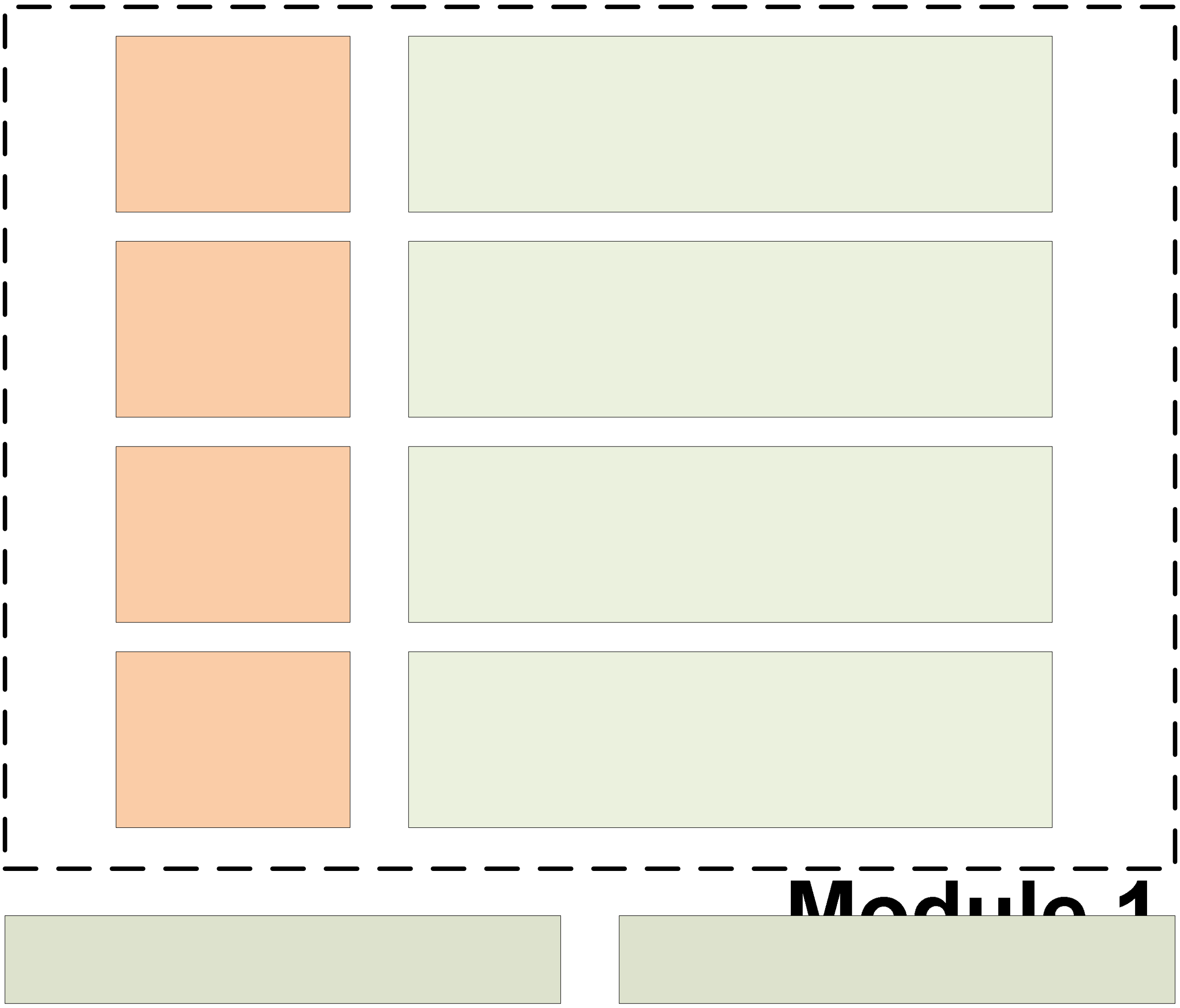

Fig. 4-Modular Platform For Integrated Assessment (MPIA) of LCBRs

Environmental Impact Assessment Module

LCA methodology was chosen to determine environmental impacts related to different LBCRs. This impact assessment will be restricted in initial developments to estimate greenhouse gas (GHG) balances using Global Warming Potential (GWP 100a) (IPCC, 2003) and energy consumption using non-Renewable cumulative energy demand (CED). This is done because other weight-based aggregation methods such as Eco-indicator 99 can cause too much noise to platform outputs due to the introduction of subjectivity. Information from Process Design Module and Process Economics Module consisting in mass and energy balances can be used to give light to some LCA methodological controversies such as non-linearity of production function and allocation problem. These two issues can be of particular importance for highly diversified pathways.

Process Economics Module

This model couples LCA outputs to DCF models in order to select optimum LCBR flowsheets according to environmental and techno-economic criteria. Ongoing research is devoted to find alternative valuation methodologies, such as adjusted present value and real options analysis, in order to adequately account for the highly dynamic nature of a multi-output system such as a LCBR, characterised by significant technologic and market uncertainties. Mutually exclusive uses of biomass feedstock will be considered for each pathway and opportunity costs will be accounted for.

Conclusions

The conceptual design of MPIA was discussed drawing a road map for its development and presenting ongoing research at the EPFL. Challenges regarding ethanol production from lignocellulosic residues and the upgrading of this pathway into a biochemical refinery are manifold: supply logistics optimisation, optimisation and selection of adequate biomass pre-treatment methods, improved integration of bioconversion processes, and development of sound pathways for the production of commodity chemicals. In general, feasibility assessments of lignocellulosic biochemical refineries (LCBR) have been focused on some of the afore-mentioned aspects, making simplification assumptions for the other, or separating environmental and economic objectives. A meaningful assessment of this kind of pathway must integrate a maximum of information regarding the whole life cycle of biorefinery products. Therefore, the MPIA must include GIS-models, semi-automated process design simulations incorporating kinetic models for chemical and biotechnological process, LCA and DCF models taking into account the highly dynamic and flexible nature of a multi-output system such as a LCBR. However, a decision support tool like this must remain flexible and user friendly and therefore a trade-off must be made between complexity and system limits.

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