A Simulation and Techno-Economic Optimization-Based Methodology to Design Multi-Product Lignocellulosic Biorefineries

Aryan Geraili, Paritosh Sharma, Robert Willis[a] , Jose A. Romagnoli*

Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA, USA
jose@lsu.edu

In this paper we present a novel methodology for joint optimization of process technologies, strategic capacity design and process operations. An iterative methodology is suggested to simulate and optimize nonlinear conversion processes and utilize process yields thus obtained to optimize the long term capacity design of process plants. This methodology is applied to a multiproduct biomass refinery that produces ethanol, succinic acid, and bio-electricity. Results indicate a reduction in strategic production capacity for each product due to the simulation, optimization, and utilization of nonlinear process yields.

1. Introduction

Owing to rapid increase in crude oil prices and concerns about its environmental impact in the past decade, efforts around the world to develop and commercialize renewable transportation fuels and biobased chemicals have intensified. Still, the commercialization of conversion technologies have been hampered by a multitude of endogenous and exogenous factors including unavailability of appropriate feedstock supply systems, lack of capital and investment risk appetite, and inefficient feedstock conversion systems. Out of all issues mentioned, optimizing conversion systems can have a tremendous impact on the overall profitability of biobased fuel and chemical value chains.

The biobased fuel and chemical conversion platforms can broadly be subdivided into 2 major pathways: (1) the biological conversion pathways including sugar- and algae-based fuels and chemicals, and (2) thermo-chemical conversion pathways that include products such as synthesis gas (gasification) and bio-oil (pyrolysis). Each pathway has been shown to have great promise, but each suffers from separate issues that prevent their commercial scale up. Thermo-chemical pathways require a large investment of capital, energy optimization and heat integration of process operations, and efficient downstream clean up and conversion processes to convert gasification/pyrolysis effluents to biobased fuels and chemicals in a profitable manner. Biological conversion pathways suffer from issues including large capital requirements for plant establishment, and inability to replicate lab-scale process yields on a commercial scale, especially yields that involve biological technologies such as enzymes and micro-organisms.

Specifically for the sugar-based fermentation conversion pathway, there is only one known commercial plant, with most demonstration scale facilities suffering from inconsistent product yields. In addition to these technical challenges, a large number of sugar platforms are essentially single-product endeavours with the intention of producing cellulosic ethanol; with ethanol being a low-margin biofuel, slight changes in input costs, process yields, or ethanol markets (prices) can have a major impact on project profitability. We believe that a truly sustainable biorefinery of the future will require a portfolio of products whose production rates can be varied to optimize plant margins based on input costs and product markets.

In this paper we propose a novel methodology to design lignocellulosic biorefineries. The methodology is based on an iterative framework that utilizes systems-based strategic planning and optimization in conjunction with mechanistic process modelling, simulation and plant optimization. The methodology is demonstrated on a multi-product biorefinery that produces cellulosic ethanol, bio-succinic acid, and bio-electricity.

2. Optimization methodology

In order to create long term value, a biorefinery has to carefully design, scale up, and operate their processing plant(s). From a modelling perspective, strategic optimization models are characterized by a few salient features including inherently long planning horizons (> 10 years) and intrinsic relationships between process variables (such as processing capacity and production rates) and economic parameters such as sales, revenue, costs, and value. In order to mathematically optimize the long term value of a biorefinery, these complex relationships have to be represented accurately without impacting the model performance significantly. While process conversion mechanisms are inherently non-linear in nature, owing to complex kinetic and thermodynamic relationships, non-linear value optimization models can quickly become complex to solve with solution performance suffering as more nonlinearities are added to a model. Consequently, LP models are suggested in this paper for the purpose of strategic planning. To overcome the mismatch between nonlinear process mechanisms and linear strategic optimization models, several decomposition strategies have been proposed in literature (Iyer and Grossmann, 1998). In this paper we will present a novel optimization methodology that attempts to model the nonlinear characteristics of process mechanisms, for the purpose of strategic optimization, in an iterative manner using process simulation and process optimization. Figure 1 shows a general representation of the proposed iterative optimization strategy. The iterative process is used to obtain a piecewise linear approximation of the nonlinear reaction- and thermo-dynamics; the nonlinear dynamics are simulated and their linear approximations are used during strategic optimization.
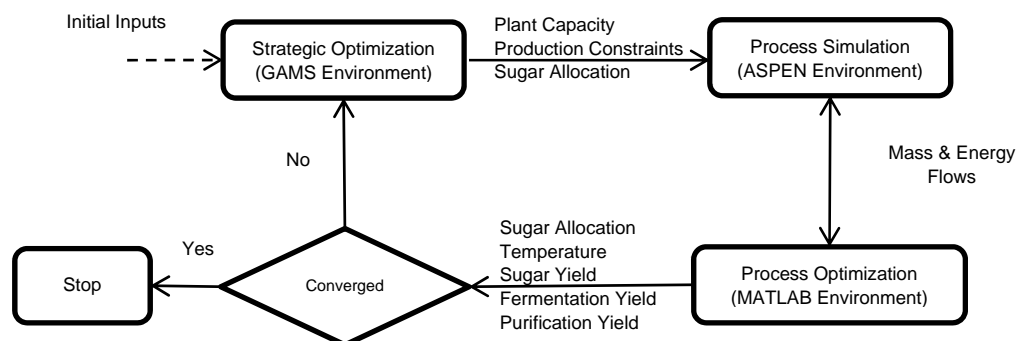

Figure 1: Optimization strategy representation

A linear programming (LP) model is proposed to optimize the project value of a hypothetical biorefinery with decision tasks that include technological superstructure design, and capacity planning. Linear black box models are utilized to represent the core technologies in a biorefinery in terms of process yields, raw material inputs, and energy loads for each technology. The nonlinearities in the black box processes are then estimated using process simulations developed using Aspen Plus. Finally the process operating conditions are optimized using a MATLAB code. The optimal operating conditions along with the simulated process yields (nonlinear) are then returned back to the strategic optimization model. This process is carried out iteratively until the optimized capacity plan (from strategic optimization) and the process yields (from process simulations) remain unchanged through one iteration.

3. Application Case Study – Lignocellulosic Biorefinery

The lignocellulosic biorefinery considered in this case study is a multiproduct plant, based on a fermentation-based sugar platform, with 3 products, cellulosic ethanol, biosuccinic acid, and bioelectricity. We assume that there is limited land available within a 100 mile radius of the plant which can be used to produce switchgrass for feedstock to the plant. The production chain comprises of 6 major systems: feedstock pretreatment, sugar hydrolysis, sugar fermentation, product purification, heat and power generation, and wastewater treatment. Each system can be executed with different technologies and at different capacities. The systems superstructure is shown in figure 2.
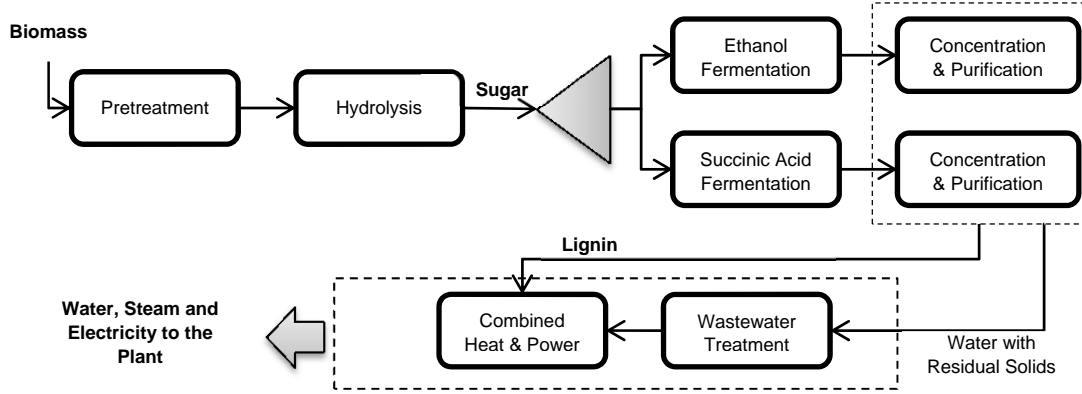
Figure 2: Block diagram for the multiproduct biorefinery plant

Technological configurations along with capital, operational, cost, yield, and energy data for biorefinery configurations are obtained from Kazi et al. (2010); these are used as starting estimates to begin the iterative optimization process. For succinic acid production, processes considered during optimization include electro-dialysis, ion-exchange and evaporative crystallization.

4. Framework Details

In this section each component of the proposed framework (figure 1) is described in some detail. While the description of the framework is based on the design of the case study presented in Section 3, each component, and the framework, can readily be adapted to other biorefining value chains.

4.1 Strategic optimization
The strategic optimization model is derived from a previously published journal paper (Sharma et al, 2012); salient components of the strategic optimization model are discussed here to give the readers a feel for the model structure and decision tasks. With respect to the integration of the strategic planning tasks and process simulation and optimization, all major process systems described in figure 2 are represented as linear black boxes in the planning model and simulated and optimized mechanistically. The major equations that are approximated linearly in the planning models and modelled nonlinearly during simulation and optimization include unit operations' yield and unit operations energy balances. These equations are provided in a condensed form below:

$$RM_{r,t} = \sum_j RM_{r,j}^{reqd} \times IN_{j,t} \tag{1}$$

$$P_{p,t} = \left(\prod_{j=1}^{n} YLD_{j,p} \right) \times BM_{j=1,t} \tag{2}$$

$$E_{j,t}^{load} = E_j^{reqd} \times IN_{j,t} \tag{3}$$

$$E_t^{Prod} = \eta \times \sum_{f,j} F_{f,j,t} \times LHV_{f,j}; \qquad E_t^{Prod} \geq \sum_j E_{j,t}^{Load} \tag{4}$$

Here, *RM* is the raw material of type r required during *t*, $RM_{r,j}^{reqd}$ is the raw material required per unit of input $IN_{j,t}$, where j is a process unit operation. Additionally $P_{p,t}$ is the annual production rate of product *p*, $YLD_{j,p}$ is the process reaction yield, $BM_{j=1,t}$ is the feedstock input, $E_{j,t}^{load}$ is the energy load of unit operation *j*, E_t^{Prod} is the total energy produced, $F_{f,j,t}$ is the fuel output of each unit operation, $LHV_{f,j}$ is the heating value of the fuel from *j*, and η is the heat transfer efficiency. Readers are directed to Sharma et al. (2012) for a complete description of the strategic optimization model. The per unit requirements ($RM_{r,j}^{reqd}$, $YLD_{j,p}$, E_j^{reqd}) are obtained iteratively from the process simulations. The cash flows (Eq. 5, Section 4.3) are calculated as the difference between the gross revenues, and raw material costs, fixed operating expenses and net taxes. For strategic planning, these the project capital costs are deducted from these cash flows, the difference is forecasted 20 years ahead and discounted back to the present to obtain the Net Present Value (NPV).

4.2 Simulation Procedure

Aspen Plus was utilized to simulate the multiproduct biorefinery with the optimal technological configuration and capacity design obtained from strategic optimization. Additional process data for simulation is based on the NREL report Kazi et al.(2010). To better estimate the nonlinear reaction dynamics of enzymatic hydrolysis and fermentation, experimentally-derived kinetic models are utilized to simulate the reactions in enzymatic hydrolysis, ethanol fermentation and succinic acid fermentation.

Kinetic Models

To consider the nonlinearity of kinetics in hydrolysis and fermentation reactions, detailed models were programmed in MATLAB. Aspen Plus is linked with MATLAB, with stream concentrations from simulation being passed to MATLAB to calculate process reaction yields; these yields are subsequently passed back to the ASPEN environment. Due to a complicated network of stream and energy recycling and integration, the simulation is rerun with the updated yield results from MATLAB to check for convergence. This process is carried out in an iterative manner until the stream concentrations from the simulation (output) match the (input) concentration values (previous iteration) to the kinetic models. The models are described briefly below.

Enzymatic Hydrolysis

A multi-reaction kinetic model developed by Kadam et al. (2004), is implemented to describe the enzymatic hydrolysis of switchgrass. This model includes reactions for: 1) decomposition of cellulose to cellobiose and glucose; 2) cellobiose hydrolysis to glucose; 3) enzyme adsorption; 4) substrate reactivity; and 5) temperature effects on hydrolysis. Langmuir type isotherms are used for the conversion of cellulose to glucose and cellobiose. Sugar inhibitions considered in this model assumes that the produced sugars can bind to the active site of the substrate and decrease the formation rate of enzyme-substrate complex.

Ethanol Fermentation

The kinetic model implemented in this study for ethanol production from sugar fermentation is based on the two substrate developed model of Leksawasdi et al. (2001), by consuming a recombinant bacteria *Z.mobilis* ZM4(pZB5), which is capable of fermenting glucose and xylose simultaneously. The model is based on the following reactions: cell growth, substrates consumption and ethanol production. Substrate and product inhibitions are incorporated to the Monod kinetic model for substrate consumptions.

Succinic Acid Fermentation

The kinetic model proposed by Song et al. (2008) for production of succinic acid from glucose by *M.succiniciproducens* MBEL55E is also implemented in this study. The main products are succinic, acetic, formic and lactic acids. A Monod equation model is developed by incorporating the excess substrate inhibition on the growth of bacteria. Additionally cell death is modeled through the concentration of organic acids that accumulate in the fermentation broth; this effect is incorporated into the cell growth model by modeling inhibition of cell growth. This model considers the conversion of glucose to acids while it is assumed that 10% of xylose is also converted; the reaction's kinetic parameters are modified accordingly.

4.3 Process Optimization

The objective function used in this study is to evaluate the annual cash flow of the process. This takes into account revenue generated from the sale of ethanol, succinic acid, and excess electricity. The direct costs include raw materials used for the production of each of these products (feedstock, enzymes, nutrients, make-up water). Labour, maintenance and transportation costs are considered as annual fixed costs. Additionally, tax credits and liabilities are also modelled to yield the after tax cash flow (objective function).

$$Cash\ Flow\ = \sum_p P_p \times Price_p\ - \sum_{r,p} RM_{r,p} \times Cost_r - \text{TC} - \text{FC} \tag{5}$$

$$Tax^{Liability} = Profit \times tax^{rate} \tag{6}$$

$$Tax^{credits} = \sum_p P_p \times Credit_p \tag{7}$$

$$Tax^{net} = \max(0, Tax^{Liability} - Tax^{credits}) \tag{8}$$

$$After-tax\ Cash\ Flow = CashFlow - Tax^{net} \tag{9}$$

5. Data Description

The input parameters used in this model are obtained from Kazi et al. (2010) and Vlysidis et al. (2011). Ethanol prices are assumed to be $2 per gallon, Succinic acid prices are assumed to be $6000 per ton and electricity prices are set at $0.05 per kilowatt-hour.

6. Results

The optimal technology superstructure obtained from strategic optimization is presented in figure 3. The mass and energy flows in figure 3 are obtained from the simulated and optimized process operations. Dilute acid pretreatment is selected along with separate hydrolysis and co-fermentation (SHCF) as this configuration yields the highest recoverable sugar, higher enzyme activity and faster conversion, respectively. The sugar stream from hydrolysis is allocated between ethanol and succinic acid for fermentation. Produced ethanol is purified by distillation and rectification columns, and dehydrated by molecular sieve adsorption, while succinic acid recovery is optimized using evaporative crystallization.
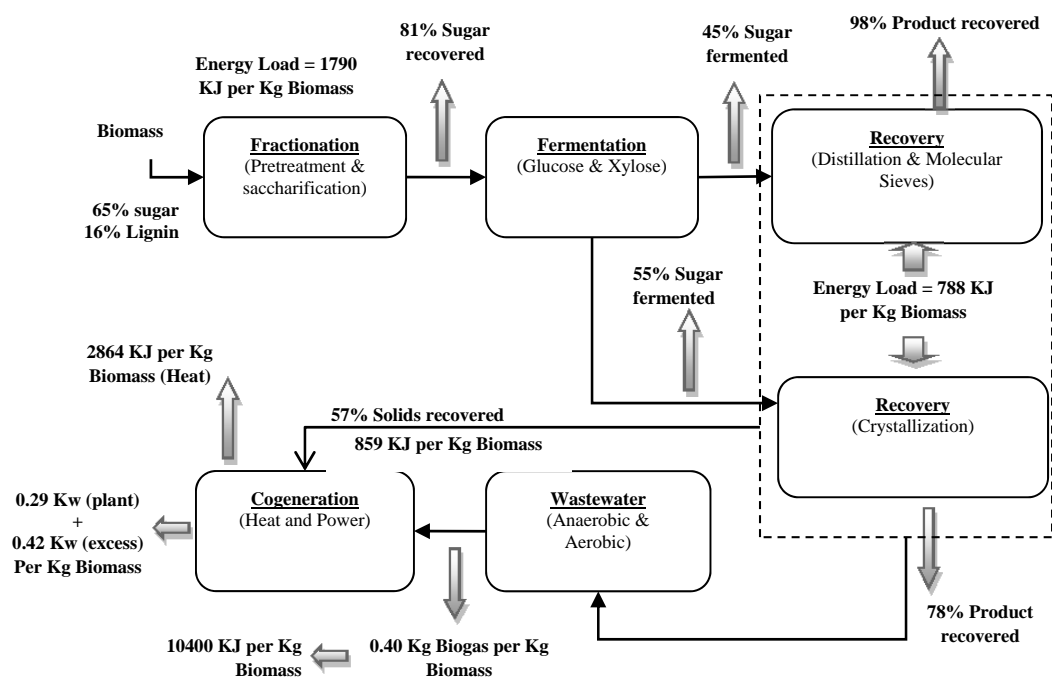

Figure 3: Optimal Process Configuration and Mass and Energy Flows

For demonstration of the methodology, two decision variables are manipulated to simulate the process and optimize cash flows and project value: (1) temperature in enzymatic hydrolysis, which its change effect on kinetic model is based on the Arrhenius Equation, and (2) sugar allocation between ethanol and succinic acid fermentation. Temperature is an important factor in enzymatic hydrolysis because the enzyme activity changes with temperature and can reduce or increase the rate of reaction. Sugar allocation impacts the fermentation reaction kinetics and consequently the fermentation yields to each product. Additionally, capacity constraints obtained from strategic optimization are used as constraints to control the processing and production rates throughout the biorefinery.

Table 1: Optimal values for selected decision variables

Temperature	49.00 °C
Sugar allocation	0.45 **(ethanol)**, 0.55 **(succinic acid)**
Cash Flow	$43 million per year
Net Present Value	$68 million

Finally, the values that are passed along from the strategic optimization model to the process simulations and received from the process optimization model are presented in table 2.

Table 2: Iteration results in optimization strategy

Parameters and Variables		Iteration1			Iteration2	
		Step 1	Step 2	Step 3	Step 1	Step 2
Capacity Constraints	Feedstock (t /y)	--	333330	--	333330	--
	Ethanol (gal /y)	--	$11082*10^3$	--	$10000*10^3$	--
	Succinic Acid (t /y)	--	15600	--	13329	--
Process Variables	Sugar Allocation	--	0.52	--	0.46	--
Yield Parameters	Sugar (kg / kg)	0.87	--	0.81	--	0.81
	Ethanol Fermentation	0.85	--	0.71	--	0.71
	Succinic Acid Fermentation	0.25	--	0.15	--	0.15
	Ethanol Purification	0.99	--	0.98	--	0.98
	Succinic Acid Purification	0.78	--	0.78	--	0.78

From table 2, it can be seen that major changes in the literature derived yield values (Step 1, Iteration 1) are noticed as the kinetic models are utilized to estimate the nonlinear dynamics of the reactions (Step 3-Iteration 1, Step 2-Iteration 2), demonstrating the utility of the proposed methodology to reconcile nonlinear process model with LP-based strategic optimization. It can be seen that while feedstock capacities remain the same through the estimation process, the optimal product capacities are reduced successively as the optimal process yields obtained from our ASPEN simulations are utilized during strategic optimization.

7. Conclusions

A novel methodology was proposed to estimate nonlinear process dynamics that occur in bioprocesses, optimize process operations and simultaneously optimize technology selection and strategic capacity design using an LP. The methodology was applied to a multiproduct biorefinery based on a sugar platform. Results show a reduction in real process yields and a consequent reduction in optimal installed capacity design for the biorefinery. For future work, this methodology will be applied to optimize strategic capacity design while also optimizing enzyme loading rates, nutrient concentrations, and product recovery.

References

IYER R. R., GROSSMANN I. E., 1998, A bilevel decomposition algorithm for long-range planning of process networks, *Industrial & Engineering Chemistry Research,* 37**,** 474-481.

KADAM K. L., RYDHOLM E. C., MCMILLAN J. D., 2004, Development and validation of a kinetic model for enzymatic saccharification of lignocellulosic biomass, *Biotechnology Progress,* 20**,** 698-705.

KAZI F., FORTMAN J., ANEX R., KOTHANDARAMAN G., HSU D., ADEN A., DUTTA A., 2010, Techno-economic analysis of biochemical production of cellulosic ethanol, *National Renewable Energy Laboratory (NREL), Technical Report NREL/TP-6A2-46588, June 2010*.

LEKSAWASDI N., JOACHIMSTHAL E. L., ROGERS P. L., 2001, Mathematical modelling of ethanol production from glucose/xylose mixtures by recombinant Zymomonas mobilis, *Biotechnology Letters,* 23**,** 1087-1093.

SHARMA P., VLOSKY R., Romagnoli J. A., 2012, Strategic value optimization and analysis of multi-product biomass refineries with multiple stakeholder considerations, Computers and Chemical Engineering. 50, 105-129.

SONG H., JANG S. H., PARK J. M.. LEE, S. Y., 2008, Modeling of batch fermentation kinetics for succinic acid production by Mannheimia succiniciproducens, *Biochemical Engineering Journal,* 40**,** 107-115.

VLYSIDIS A., BINNS M., WEBB C. , THEODOROPOULOS C., 2011, A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals. *Energy,* 36**,** 4671-4683.