

# Modeling and optimization of a bioethanol production facility

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**Abstract** The overall objective of this study is to identify the optimal bioethanol production plant capacity, configuration, and operating conditions, based on currently available technology for all the processing sections involved. To effect this study, a systematic method is utilized which involves the development of a process flow-sheet and superstructure for the overall technology selection. It also includes simulation as well as mathematical model development for each processing step. The optimality of each process pathway is determined via economic analysis. The developed optimization model also incorporates various biomass feedstocks as well as realistic upper and lower limit equipment sizes thereby ensuring pragmatism of the work. For this study, the criterion for optimization is minimum ethanol price. The secondary objective of this study attempts to mathematically model the seasonal variation in availability of biomass feedstock. This sub-model is incorporated into the overall model and economic evaluations done to determine the minimum ethanol selling price and optimal plant capacity.

**Keywords** Biofuels · Biomass · Optimization · Economics · Sustainability

## Introduction

The United States is heavily dependent on foreign oil. According to the Energy information administration (EIA), importation represents forty-nine percent (49 %) of the United States' current use of crude oil and refined products. To reduce this dependence on foreign oil which in itself continues to slowly dwindle, the US government proposed mandates such as the “Energy Independence and Security Act of 2007” (Sissine 2007). This mandate requires an increase in the amount of renewable fuels to 36 billion gallons by the year 2022. The primary renewable fuel initiative before this mandate was the “Energy Policy act of 2005”. This policy required a production increase to 15 billion gallons ethanol by the year 2015.

The support for the increased use of biofuels does not only solely hinge on the need to reduce foreign oil dependence but also on its potential environmental benefits. The use of biofuels as opposed to the conventional fossil fuels can result in a reduction in carbon dioxide emissions which is one of the major gases touted as a contributor to global warming. Other advantages include the ease of using current infrastructure for fuel distribution as well as its ability to reduce engine knock. There has been extensive discussion on the merits, drawbacks, and hurdles for promoting the production of biofuels (e.g., Sanaei et al. 2013; Chouinard-Dussault et al. 2011; Wenzel 2009). In addition, ecological and safety issues of biorefineries have also been discussed in the literature (e.g., Honnery et al. 2013; El-Halwagi et al. 2013).

The ethanol production industry is dominated by the use of first generation feed-stocks. These first generation materials are food sources and consequently increase pressure on supply chains catering for population demands. This growing food and fuel competitive dilemma drives the

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renewable fuel industry to delve into scientifically uncharted territory to devise bio-processing routes that are more technologically efficient and versatile. The direct result of these efforts has spawned the so-called second generation biofuel feedstocks, namely ligno-cellulosic biomasses. These materials have gained traction in the biofuel industry not only for their potential to fully displace first generation feedstocks but also for their higher ethanol yields. The latter factor has a tremendous impact on the overall fossil fuel displacement as well as reducing greenhouse gas emissions. The high ethanol yield also helps to increase optimal plant capacity as compared to first generation feedstocks.

There are currently various technical and economic barriers that prevent implementation of second generation ethanol processes. In this study, we seek to explore the benefits of mathematical optimization in providing solutions to a potentially game changing fuel source.

There are currently numerous routes for converting biomass sources into biofuels though economics define the development and use of such technology. Overviews of biomass-to-biofuel processing pathways and technologies are available in literature (Kamm et al. 2006; Clark and Deswarte 2008; Basu 2010; Cardona et al. 2010; Pham and El-Halwagi 2012; Stuart and El-Halwagi 2013). For bioethanol production facilities, the overall economics are heavily dependent on feedstock cost, chemical cost, plant capacity, and selected technology or processing associated costs. The latter economic factor is normally critical to the overall design of a bioethanol facility since its performance would dictate the overall production of valuable end product. In most cases the development of a bioethanol facility hinges on the proper selection of technology that insures the highest and most cost-effective performance. This selection process is not intuitive since there are many possible technology routes that are difficult to economically evaluate for every possible plant capacity. These complexities pose serious challenges for the design engineers in charge of technology selection, capacity determination, and flow-sheet optimization.

Several approaches have been adopted for the design of bioethanol facilities. The most commonly used approach is design through analysis (Cardona and Sánchez 2007; Ojeda et al. 2010; Ojeda et al. 2011; Conde-Mejía et al. 2012; Kazi 2010). According to this approach, a base case for the plant or a section of the plant is selected and designed based on the experimental data and simulation models. Various scenarios are analyzed and a techno-economic or energy analysis is used to select the final design. A recent approach is based on the development of superstructures that embed potential process configurations of interest and using optimization to select from among the alternatives. Previous works by (Martín and Grossmann 2010) have

focused on utilizing this strategy to produce bioethanol via syngas obtained from biomass gasification. In contrast this study utilizes a similar strategy though focuses on bioethanol production via other biochemical pathways.

To achieve this task, literature reviews were done to gather data on the many available processing routes currently utilized in the industry as well as those not commercially available. Next, a superstructure depicting all the possible routes is developed and an optimization model is formulated to solve the technology and feedstock selection problem.

Previous studies have focused on utilizing single values for conversions and simple relationships for product separation to allow for large model development with relatively short computational times (Martín and Grossmann 2011; Martín and Grossmann 2012). These choices enable the development of efficient optimization approaches. In this study, we use a hierarchical approach to screening and design where appropriate levels of details are provided as needed. Furthermore, instead of using reaction pathways with single-value conversions, we utilize experimentally based mathematical equations that relate conversions to operating parameters and separation costs to varying flow-rates and compositions. This approach provides the insights for the validity of chosen conversions or the possible tradeoffs for reduced conversions as a function of varying plant capacities. The study also provides and utilizes a simple mathematical storage model that linearly relates biomass harvesting rate to plant capacity.

For the economic evaluation, the model includes mathematical relations for equipment cost, feedstock cost, and overall processing costs. An economic analysis is performed to determine the minimum ethanol selling price that also provides maximum profits. The optimization model is applied to a realistic case study where feedstock cost varies and seasonal availability requires the use of biomass storage. The data generated is used to identify the optimal plant capacity and storage conditions for a typical bioethanol facility.

The overall model is limited to optimizing the economics for the optimal plant capacity. It does not take into consideration the ecological impacts on optimal plant capacity. Other studies have illustrated these effects (Gwehenberger et al. 2007) and can serve as a good basis for extending this model in future works.

## Process description

The process utilized in this study for techno-economic analysis is based on an altered model outlined by NREL (Aden 2002). For this study, the process consists of eight processing sections namely, feedstock size reduction and storage, pretreatment and hydrolyzate conditioning, enzymatic hydrolysis,

co-fermentation, ethanol product separation and recovery, wastewater treatment, biomass waste combustion and cogeneration.

#### Feedstock and size reduction

The location of a biorefinery is typically dependent on the local feedstock cost, availability, and chemical quality. The latter is crucial to the process since the maximum production of the valuable product is dependent on the chemical content of the feed. For this study the choices of feedstock were corn stover, switchgrass, and poplar wood. All feeds are promising ligno-cellulosic material for bio-fuels and reduction in GHG emissions (Farrell et al. 2006).

Size reduction of the biomass is employed to increase the overall surface area of the biomass for pretreatment and subsequent enzymatic hydrolysis. In this study, the electrical energy cost for size reduction (Mani et al. 2004) was incorporated to insure completeness of the study and to illustrate the potential for co-generation in biorefineries.

#### Pretreatment

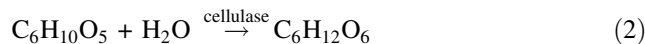
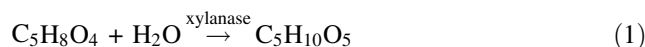
The pretreatment step in bioethanol production is the most performance determining step of the facility. This step represents a physiochemical, chemical or thermochemical breakdown of the biomass so that the encapsulating effect of the lignin is reduced and as such, enzymatic hydrolysis is improved. (Chang et al. 1997) To achieve this, there are many pretreatment techniques that have been developed by the scientific community, some of which are currently commercial. In many cases, the techniques developed are difficult for scale up and lack the necessary data for a proper economic analysis therefore this study focuses on those that are practical, show great potential, and are well-documented in the literature. For this study the pretreatment routes chosen were:

- Ammonia fiber explosion (AFEX)
- Dilute acid
- Lime
- pH controlled liquid hot water (LHW)

The required time and conditions for effective pretreatment is evidently different for each process. This study consequently focuses on optimizing these parameters so as to balance the performance and economics.

#### Enzymatic hydrolysis

Once the biomass has been pretreated, it is then conditioned and passed to the enzymatic hydrolysis step. In this step, enzymes are used to convert polysaccharides into its constituent C5 and C6 reducing sugars which are easily converted to ethanol in the fermenting step.



In the hydrolysis reaction, the enzymes bind to the biomass to achieve the conversion. This process results in some bonds being irreversible and consequently enzyme loss increases in the following solid separation step. The eventual cost of the hydrolyzing enzymes for a poorly designed process consequently increases and in many cases can tip the scales of economic viability for the entire bio-processing route. For this study, centrifugation followed by ultra-filtration was used to recover the enzymes as outlined in the literature (Steele et al. 2005).

#### Fermentation

This step is a very simple and well-researched process. It involves the conversion of the C5 and C6 reducing sugars into ethanol via enzymatic action. For this study, the co-fermentation is used whereby simultaneous fermentation of C5 and C6 sugars is carried out in a single step. The advantage of this technology is a reduced operating and equipment cost associated with the process.

#### Separation and recovery

Once the fermentation step achieves maximum conversion of sugars into the desired ethanol product, there is a need to recover the ethanol from the dilute broth. This process is one of the most energy intensive sections due to the high water content of the fermentation broth. For this study the preferred scheme incorporated the use of a stripping column following by a distillation column and subsequently, molecular sieve beds. Other possible schemes utilize extractive distillation instead of molecular sieve beds though for this study it was excluded as an option in the process synthesis framework.

For this study, the stripping column is located upstream of the distillation column so as to pre-separate any unknown high molecular weight compounds as well as particulates from the preceding section. It also insures that the water stream from the bottom of the distillation column can be recovered and recycled to the front end of the process with little to no-required treatment.

Another attractive factor for the scheme decision was the convenience in being able to supply the stripping column with steam from the waste water evaporator.

#### Problem statement and objectives

Given is the requirement for an economically feasible bioethanol production route. Available for consideration

are a number of feedstocks ( $N_f$ ) and processing technologies ( $N_p, N_h$ ). It is desired to develop a systematic procedure for identifying the optimal bioethanol production pathway based on available literature and commercial data. There are numerous challenges in identifying the solution which require answers to the following questions:

- Which feedstock(s) should be used and how much should be fed to the process?
- Which bio-processing technologies should be utilized and what are the optimal operating parameters?
- What processing capacity minimizes the cost of bioethanol and also maximizes profits?
- Which processes are least affected by raw material and or chemical costs?
- How does biomass storage affect the optimal plant capacity?

## Approach

To achieve the aforementioned objectives the following key procedural steps were undertaken for the development of the overall optimization model:

- Development of a process superstructure that defines all possible pathways taken from biomass to ethanol
- Development of a general processing scheme that includes details for each processing unit (Fig. 1)
- Simulation of each processing unit and development of mathematical models that describe its operation
- Development of equipment costing models for units that do not follow the sixth tenth rule

A detail process flowchart depicting these procedural steps is shown in Fig. 2.

### Superstructure and process development

The given route decisions for the superstructure as illustrated in Fig. 3 are simplified as follows:

- A selection of biomass feedstock
- A selection of pretreatment technology along with its corresponding hydrolysis unit
- A common co-fermentation process
- A common ethanol separation and recovery process

For this study, there is only one designed process for the co-fermentation section as well as the product recovery. This evidently limits the optimization model to biomass, pretreatment, and hydrolysis process selection.

The process flow diagram was adapted from many schemes illustrated in literature along with basic knowledge of process design.

As shown, the process incorporates basic energy and mass integration of all processing units. The pretreatment shown is dilute acid though many other pretreatment processes were developed and incorporated into the optimization model.

### Simulation and nonlinear models

In this study, the energy and material flows are allowed to vary due to other varying parameters in the optimization model. Consequently, simulating an entire bio-processings scheme offers little information for the overall optimization model.

Therefore simulation software was used to provide material and energy flow data for each unit operation. This simulation data was then used to develop linear and nonlinear mathematical models that accurately describe or track the material and energy flows. For this effort, ASPEN PLUS<sup>®</sup> was used as the simulation software. To account for the components in biomass that are not represented in ASPEN PLUS<sup>®</sup>, EXCEL spreadsheet calculations based on literature data were performed.

The core of this optimization problem relies on the ability to characterize each unit operation mathematically so as to develop an overall model that reflects a configuration based on the optimal choice of operating parameters. To obtain these mathematically characteristic models, experimental values are extracted from literature (Chang et al. 1997; Dien et al. 1997; Esteghlalian et al. 1998; Kim et al. 2003; Alizadeh et al. 2005; Kim and Holtzapple 2005; Mosier et al. 2005; Teymouri et al. 2005) and a nonlinear regression model is developed.

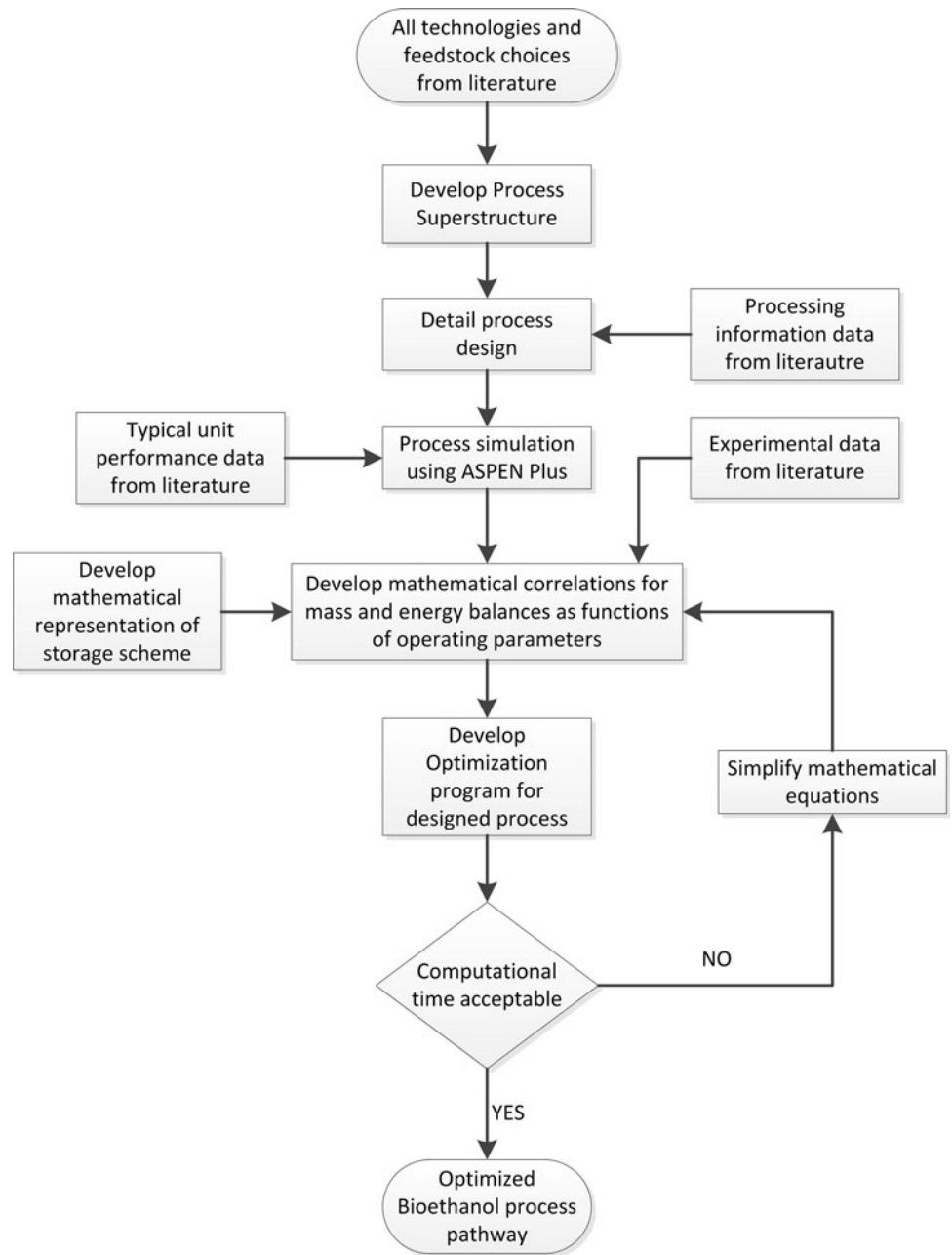
In most cases these models predicted the experimental data within  $\pm 5\%$  error while in other cases the predictions were not as accurate. In cases where nonlinear models were overly complicated to the point that an optimal solution may be hindered, experimental data were represented as a group of linear equations. These linear equations are then incorporated into the model via the convex hull formulation. The optimization formulation to determine the nonlinear model is as follows:

$$\min \|y - y^*\|_2^2 \quad (3)$$

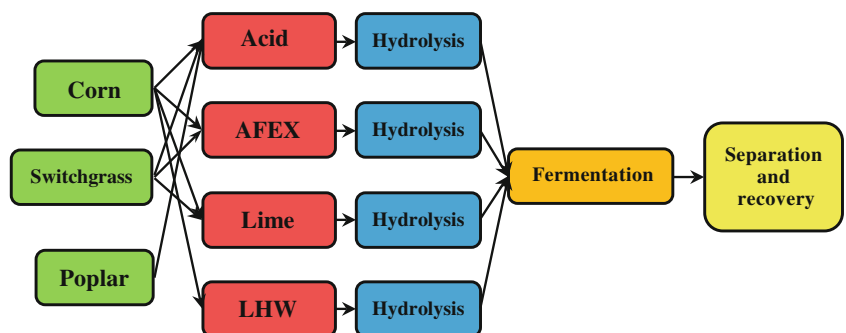
This formulation represents the minimization of the summation of the square of the absolute error between the predicted ( $y$ ) and experimental value ( $y^*$ ). The predicting equation is based on the shape and characteristics of the experimental graphs then tested using the above optimization formulation for the least possible percent error. By minimizing the percent error, the accuracy and validity of the predicted equations is insured. Table 1 shows some of the linear and nonlinear models used for this study while Figs. 4 and 5 show an example of the accuracy of some of the models utilized.



**Fig. 2** Process flowchart



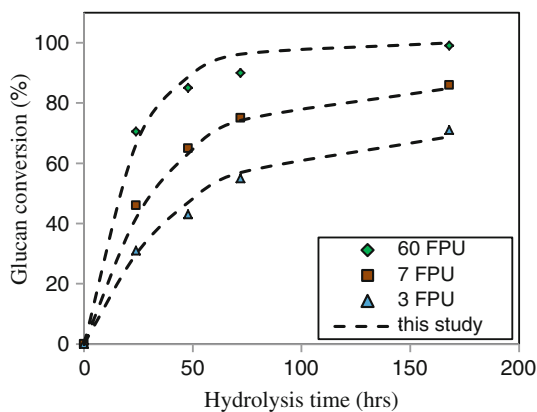
**Fig. 3** Superstructure for bio-processing pathways



**Table 1** Process units' linear and nonlinear mathematical correlations

Processing unit	Biomass	Correlations	Equation no.
AFEX pretreatment	Corn stover	$X_G = A[1 - \exp(-k_G t_h)]$	(4)
		$A = 48.6 + 51.4[1 - \exp(-0.182 \text{ FPU})]$	(5)
		$k_G = 0.018(\text{FPU})^{0.2263}$	(6)
Fermentation	All	$X_{\text{glu}} = 100[1 - \exp(-k_{\text{glu}} t_f)]$	(7)
		$X_{\text{xyI}} = 100\{1 - \exp[-(k_{\text{xyI}} + k_{\text{tol}}) t_f]\}$	(8)
		$X_{\text{tol}} = 100[k_{\text{tol}} / (k_{\text{xyI}} + k_{\text{tol}})]\{1 - \exp[-(k_{\text{xyI}} + k_{\text{tol}}) t_f]\}$	(9)
		$k_{\text{glu}} = 0.521[E]^{0.2229}$	(10)
		$k_{\text{xyI}} = 0.011[E]^{0.4464}$	(11)
		$k_{\text{tol}} = 0.001[E]^{0.1373}$	(12)
Stripping column	All	$F_{\text{LPS}} = 0.081 F_{\text{cont}} + 0.185 F_{\text{H}_2\text{O}} + 0.223 F_{\text{etoh}} + 1.347$	(13)
Distillation column	All	$Q_{\text{cond}} = 1.458 F_{\text{etoh}} + 0.073 F_{\text{H}_2\text{O}}$	(14)
		$Q_{\text{reb}} = 1.435 F_{\text{etoh}} + 0.077 F_{\text{H}_2\text{O}}$	(15)
Waste water evaporator	All	$F_{\text{MPS}} = 0.389 F_{\text{H}_2\text{O}} - 0.321 F_{\text{cont}}$	(16)
		$F_{\text{LPS,r}} = 0.336 F_{\text{H}_2\text{O}} - 0.314 F_{\text{cont}}$	(17)
		$A_{\text{evp}} = 0.057 F_{\text{H}_2\text{O}} - 0.049 F_{\text{cont}}$	(18)

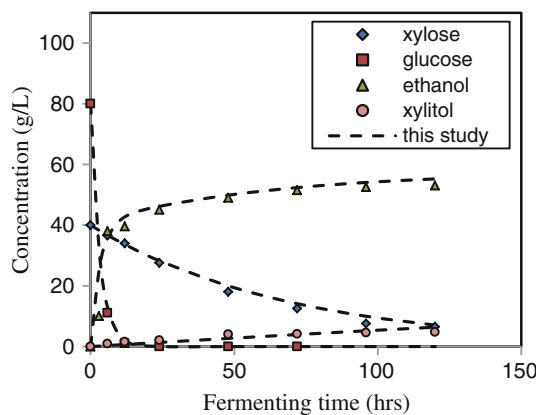
$A_{\text{evp}}$  total evaporator area ( $\text{m}^2$ ),  $[E]$  fermenting enzyme concentration (dry g/L),  $\text{FPU}$  filter paper unit enzyme loading,  $F_{\text{LPS}}$  flow of low pressure steam to unit (kg/hr),  $F_{\text{MPS}}$  flow of medium pressure steam to unit (kg/hr),  $F_{\text{cont}}$  flow of sugars/contaminants to unit (kg/hr),  $F_{\text{H}_2\text{O}}$  flow of water to unit (kg/hr),  $F_{\text{etoh}}$  flow of ethanol to unit (kg/hr),  $F_{\text{LPS,r}}$  recycle flow of LPS from unit (kg/hr),  $Q_{\text{cond}}$  distillation column condenser duty (kW),  $Q_{\text{reb}}$  distillation column reboiler duty (kW),  $t_h$  hydrolysis time (hrs),  $t_f$  fermentation time (hrs),  $X_G$  conversion of glucan (%),  $X_{\text{glu}}$  conversion of glucose to ethanol (%),  $X_{\text{xyI}}$  conversion of xylose to ethanol (%),  $X_{\text{tol}}$  conversion of xylose to xylitol (%)



**Fig. 4** Glucan conversion of AFEX pretreated corn stover (Teymouri et al. 2005)

Due to the limited availability of experimental data, the pretreatment and hydrolysis process are lumped together resulting in some regression models being based on pretreatment time, hydrolysis time, enzyme loading, or a combination of all three parameters.

The optimization program is developed to allow for varying plant capacities and unit input compositions. To account for this dynamic the separation and recovery units were modeled to correlate with the various feed flow rates and compositions. These correlations provided information for operating costs as well as unit capital costs.



**Fig. 5** Fermentation at 2 g/L enzyme concentration (Dien et al. 1997)

**Cost analysis**

To obtain capital cost estimates, ASPEN Process Economic Analyzer and literature data (Peters et al., 2003; Kazi 2010; El-Halwagi 2012) were used. To insure fair comparison among cost estimates, all values obtained were updated to 2011 US dollars.

To account for operating costs associated with the process, commodity prices of the various chemicals used are obtained from ICIS. Cost of steam and other non-chemical

operating expenses are obtained from literature (Kim et al. 2003) or governmental databases.

### Case study I

This case study simply represents the base case optimization model. By utilizing mathematical models as illustrated in Table 1, the overall optimization framework was developed for the general processing scheme resulting in a Mixed Integer Nonlinear Programming (MINLP) problem. To solve this problem, the LINGO<sup>®</sup> optimization software was used (Schrage 2006). To insure fast results, the MINLP problem was decomposed into Nonlinear Programming (NLP) sub-problems to identify the optimal pathway.

To insure pragmatism of the work, each unit operation was given a set of design parameters that were deemed acceptable in the industry and utilized in the literature (Kazi 2010). For this study, constraints were placed on all processing units namely, the pretreatment and hydrolysis section, the fermentation section as well as the ethanol separation and recovery section. A curt list of the typical

**Table 2** Design parameters for pretreatment and hydrolysis

Process	Parameter	Value	Units
Acid	SL	30	wt%
	Acid conc.	0.6–1.2	wt%
	Time	0–15	mins
	Temperature	140–180	°C
	HL	7	wt% glucan
	EL	0.24	ml/g glucan
AFEX	SL	50	wt%
	Time	5	mins
	Temperature	100	°C
	HL	7	wt% glucan
	EL	0–100	FPU/g glucan
	Lime	Water load	9–10
Lime load		0.1	kg/kg bio.
Time		2	hrs
Temperature		120	°C
HL		150	g bio/kg H <sub>2</sub> O
EL		0–100	FPU/g glucan
LHW	SL	16	wt%
	Time	0–30	mins
	Temperature	190	°C
	HL	7	wt% glucan
All	EL	10	FPU/g glucan
	HT	0–168	hrs

SL solid loading, HT hydrolysis time, EL enzyme loading, HL hydrolysis load

**Table 3** Design parameters for fermentation process

Parameter	Value	Units
Enzyme load	0.1–2	Dry wt protein/L
Time	0–120	hrs
Temperature	50	°C
Volume	0–4,000	m <sup>3</sup>

**Table 4** Design parameters for separation and recovery process

Equipment	Parameter	Value	Units
Stripper	Pressure	10	psig
	Size	2–12	ft
	Height	35	ft
Distillation	Size	2–12	ft
	Height	90	ft
Evaporator	1st effect	30	psig
	Area	0–9,680	ft <sup>2</sup> /effect

**Table 5** Chemicals costs

Chemical	Value	Units
Acid	50–94	\$/short ton
Ammonia	500–771.64	\$/1,000 kg
Lime	56–74	\$/short ton

**Table 6** Plant utility costs

Utility	Value	Units	
Natural Gas	4.4	\$/MMBTU	
Electricity	0.08	\$/kWh	
Steam	6.61	\$/1,000 kg	
Water	Process	0.001	\$/m <sup>3</sup>
	Cooling	0.065	\$/m <sup>3</sup> circulating
Waste	36	\$/1,000 kg	
Labor	27.60	\$/hr	

**Table 7** Biomass gate cost

Biomass	Value	Units (Kg)
Corn stover	61.6	\$/1,000
Switchgrass	81.5	\$/1,000
Poplar	101.6	\$/1,000



parameters and constraints used are shown in Table 2, 3, and 4.

Economic variables

The overall objective of the optimization model was set to minimize the production price of ethanol. As such current estimates on chemical and non-chemical costs for the overall process are crucial for accurate results. For this study, Table 5, 6, and 7 list some of the costs used.

The cost of biomass to a refinery is especially critical in the overall economic analysis of the process. In many regards this cost is based on geographical location, farmer premium or land rent, fertilizer cost, farming cost, harvesting, and collection as well as transportation cost. For this study the method for determining this cost was adapted from literature (Huang et al. 2009).

For this study an overall plant life of 10 years was established considering the high risk involved in biorefinery projects. A corporate tax rate of 25 % along with an interest of 7 % was also incorporated into the economic analysis. A working capital of 15 % of total capital investment (Kim et al. 2003) as well as straight line depreciation with no salvage value was also assumed.

Case study II

The premise of this case study is to offer an insight into the economics involved in the storage of biomass for later processing due to climatic changes that may hinder harvesting and biomass growth. In this analysis a simple mathematical model is proposed and integrated into the base case model for the best configuration determined from case study I. To illustrate the applicability of the model, some extreme cases would be used to define regions of feasibility for using storage as a bio-processing option.

Model formulation

The concept of the model is based on the simple principle involved when filling and emptying a storage unit. To include the decomposition of the biomass over time of storage a rotting or decomposition rate is included in the formulation. The model development is done for two periods of the year—the harvesting and drought or winter period. In the first period, the biomass is harvested and sent for storage while the plant continues to operate utilizing this stored biomass. Hence there is an accumulation rate over time in the storage facility. During the winter period, harvested biomass supply to the storage facility is negated and stored biomass continues to be used until the start of

the harvesting period of the next year. The overall mass balance on the storage facility for the harvesting and winter periods are given by Eqs. 19 and 20, respectively.

$$\frac{dM_{S1}}{dt} = \dot{m}_H - \dot{m}_P - rM_{S1} \tag{19}$$

$$\frac{dM_{S2}}{dt} = -\dot{m}_P - rM_{S2} \tag{20}$$

where,

- $M_{S1}$  Mass of biomass in storage facility at any given time during harvesting period
- $M_{S2}$  Mass of biomass in storage facility at any given time during winter period
- $\dot{m}_H$  Harvesting rate during harvesting period
- $\dot{m}_P$  Plant biomass capacity
- $r$  Biomass decomposition/rotting rate
- $t$  Time variable (months)

In the mass balance the rotting rate is considered to be a function of the total mass stored at a given time. It is defined as the fractional loss of stored mass per month due to decomposition or polysaccharide loss as a result of microorganism digestion. These mass balances are evidently first-order differential equations with their respective solutions represented by Eqs. 21 and 22.

$$M_{S1} = \frac{\dot{m}_{acc}}{r} [1 - \exp(-rt_1)] \tag{21}$$

$$M_{S2} = M_s^o \exp(-rt_2) - \frac{\dot{m}_P}{r} [1 - \exp(-rt_2)] \tag{22}$$

where,

- $M_s^o$  Accumulated mass in storage facility at the end of the harvesting period ( $t_1 = t_{har}$ )
- $t_1$  Time variable within harvesting period ( $0 \leq t_1 \leq t_{har}$ )
- $t_2$  Time variable within winter period ( $0 \leq t_2 \leq t_{win}$ )
- $\dot{m}_{acc}$  Biomass accumulation rate during harvesting period ( $t_1 = t_{har}$ )

To determine the relationship between the harvesting rate during the harvesting period and the overall biomass plant capacity, the following mathematical relationships are understood:

$$M_s^o = \frac{\dot{m}_{acc}}{r} [1 - \exp(-rt_{har})] \tag{23}$$

$$0 = M_s^o \exp(-rt_{win}) - \frac{\dot{m}_P}{r} [1 - \exp(-rt_{win})] \tag{24}$$

$$t_{har} + t_{win} = 12 \tag{25}$$

where,

- $t_{har}$  Total harvesting period
- $t_{win}$  Total winter period

By simplifying the exponential terms with constants since the harvest and winter period are known,

$$c_1 = [1 - \exp(-rt_{\text{har}})] \quad (26)$$

$$c_2 = [1 - \exp(-rt_{\text{win}})] \quad (27)$$

The relationship between the harvesting rate and plant capacity is given by:

$$\dot{m}_P = \frac{c_1(1 - c_2)}{c_2 + c_1(1 - c_2)} \dot{m}_H \quad (28)$$

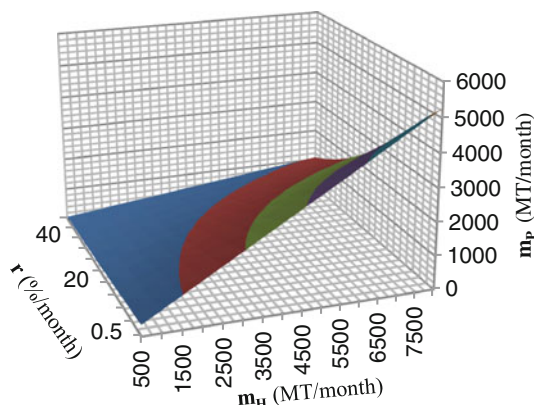
This developed linear relationship can be easily integrated into the entire optimization program and be used for any harvesting and winter period and desired rotting rate. The equation though breaks down if the rotting rate is selected as zero due to the exponential terms used. In essence the use of a very small number would give the same accurate value as the formulation if the rotting rate were not incorporated into the model. Figure 6 illustrates the overall relationship among rotting rate, harvesting rate and plant capacity.

To investigate the economics of biomass storage there are two scenarios for which the plant can operate.

### Scenario 1

Operate the plant during the harvesting period only with a shut down or turn down during the winter period, where there is no biomass available for ethanol production. Therefore the plant capacity is simply equal to the harvesting rate. Assumptions are as follows:

- 1 The plant operates at the full number of harvesting days with maintenance and upgrades being performed during the shutdown or turn down period
- 2 During shut down period, labor is cut to 80 % of the required labor force for full capacity to allow for



**Fig. 6** Graph showing relationship between plant biomass capacity and harvesting rate ( $t_{\text{har}} = 9$  months)

maintenance work and to ready the plant for restart come harvesting period. The plant utilities are also reduced to 60 % of normal operating capacity

### Scenario 2

Operate the plant year round based on the operating days selected in the base case with constant storage of biomass to supply the plant with feed for the winter period. Assumptions are as follows:

- 1 The plant operates for 329 days of the year (90 % operational factor)
- 2 Storage of biomass is done using an open field with rental rates obtained from literature (William 2011)
- 3 The average rotting rate of biomass is 10 % lost over a 2 month period to account for open-air storage
- 4 The base case winter period for storage would be 3 months with a remaining harvesting period of 9 months
- 5 The lost biomass that decomposes is resold as compost at 90 % of the original gate price

## Results and discussion

### Case study I

The optimization model for this study indicated that the optimal bioethanol facility configuration incorporated the use of corn stover as a feedstock with an AFEX pretreatment configuration as illustrated in Fig. 7. These results run contrary to current industrial processes which mainly incorporate dilute acid as the pretreatment of choice. Consequently the results buttress the notion that heuristics and industrial best practices alone cannot insure optimal process synthesis.

The model also indicates that the minimal ethanol production price based on this processing route is \$1.96/gal which fairs well with other studies focusing on bioethanol production. The minimal ethanol price based on other configurations studied is illustrated in Fig. 8. The graph indicates that the optimal plant capacity for the base case optimal configuration lies between 2,000 and 4,000 MT/day of biomass, a result also indicated in other studies though for different biomass sources. Beyond this plant capacity, the minimal cost of ethanol increases which is evidently due to increased cost of transportation.

To highlight the differing parameters required for optimality for each configuration, Table 8 illustrates operational and economic data for each processing scheme. This data further supports the idea that for bioethanol facilities, the transportation cost hinders the advantages of economies of

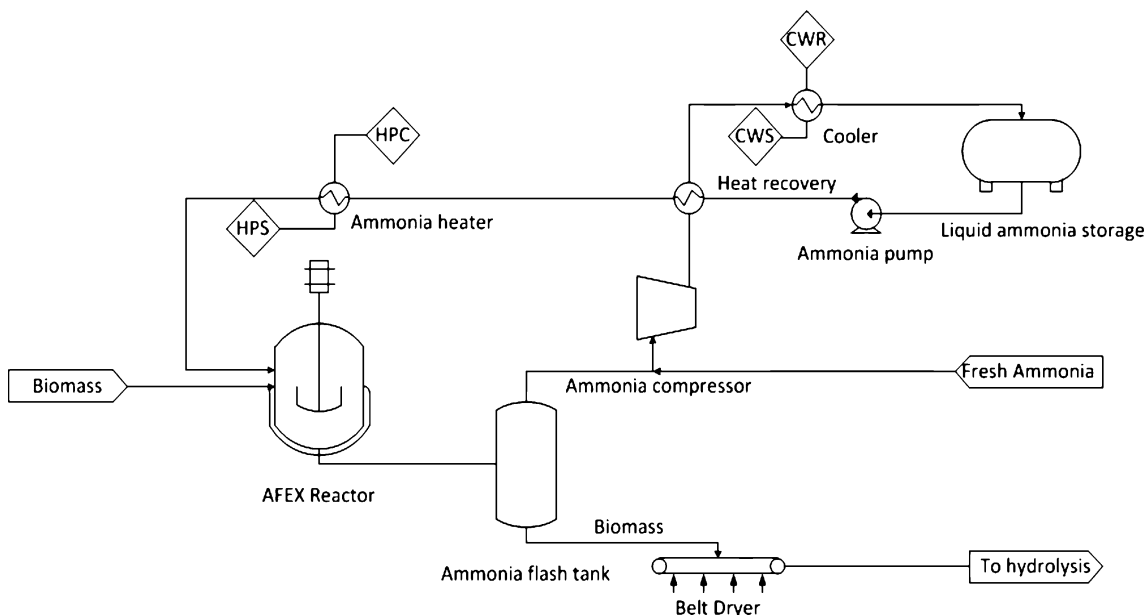


Fig. 7 AFEX pretreatment

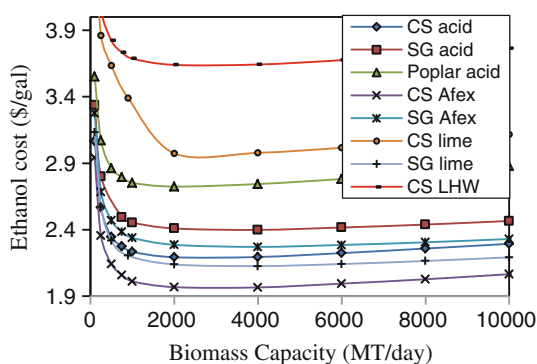


Fig. 8 Effect of plant capacity on ethanol price

scale as indicated in Fig. 8. For the corn stover and AFEX pretreatment configuration, it was determined that the hydrolysis enzyme loading mimics the variation with plant capacity as seen with ethanol price. A closer look at both graphs reveals that the minimal loading does not align with the minimal ethanol price. This finding illustrates that the improved performance and profit benefit of an increased enzyme loading outweighs the cost implications (Fig. 9)

Sensitivity analysis

To insure that the bioethanol process survives in present economic markets, a sensitivity analysis was done to project its ability to withstand fluctuating feedstock and chemical prices. Figure 10 shows the upper and lower bound regions of minimum ethanol prices for three of the best configurations based on the upper and lower price of

pretreatment chemical. It should be noted that the upper bound of the acid pretreatment configuration would incorporate two fluctuating chemicals—acid and lime. The latter chemical is used to neutralize the spent acid from the pretreatment section.

An analysis of this graph indicates that the lime pretreatment configuration using switchgrass is the most stable due a fairly invariant chemical price.

The highest variance is seen with the AFEX pretreatment configuration which is as a result of the high cost of ammonia.

Case study II

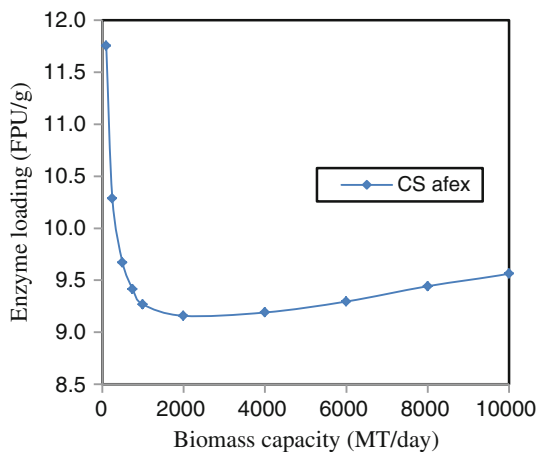
The economics surrounding the storage of biomass via the use of the seasonal variation model is illustrated in Fig. 11. This graph shows that the use of storage due to biomass unavailability significantly affects the minimum ethanol selling price despite the fairly inexpensive cost of storage. It also indicates that at the base case, storage is more economical than the non-storage approach up to a specific plant capacity. This breaking point where storage is no longer considered economical is at a plant capacity of 98 MMgal/yr–3,750 MT/day biomass plant with storage or a 4,500 MT/day plant without storage.

The high storage cost sensitivity analysis was done using a cost function obtained from literature (Kazi 2010) that describes the use of a concrete pad for storing biomass. It was assumed that the use of this pad reduces the decomposition rate of the biomass by five fold since it is not in contact with the earth.

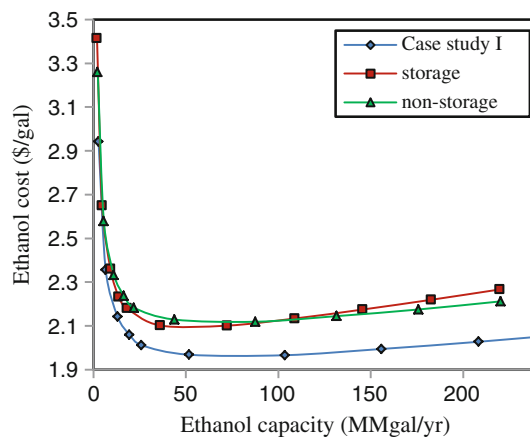
**Table 8** Optimal conditions for selected schemes

Process	C. stover AFEX	S. grass lime	C. stover acid	S. grass AFEX	S. grass acid	Poplar acid	C. stover lime	C. stover LHW
Plant cap. (MT/day)	2,788	3,978	2,717	3,865	3,559	1,824	3,274	2,635
Xylan conv. (%)	58.36	98.42	88.67	70.53	89.85	90.99	57.49	62.04
Glucan conv. (%)	89.44	78.37	84.53	95.14	84.54	89.74	59.51	71.56
Pretreat time (mins)	5	120	0.51	5	0.41	0.33	120	12.38
Acid conc. (wt%)	–	–	1.20	–	1.20	1.20	–	–
Pretreat temp. (°C)	100	120	180	100	180	180	120	190
Hydrolysis time (hrs)	155.4	73.2	104.0	168.0	104.2	117.2	168.0	48.0
Fermenting time (hrs)	120.0	120.0	120.0	119.2	120.0	120.0	120.0	120.0
FCI (\$MM)	129.25	236.38	136.34	164.77	164.65	101.77	211.44	281.37
EtOH cap. (MMgal/yr)	72.1	102.2	75.4	101.5	92.8	52.9	62.4	58.5
EtOH cost (\$/gal)	1.956	2.124	2.184	2.267	2.396	2.724	2.959	3.627
Enzyme cost (\$/gal)	0.412	0.324	0.941	0.537	0.896	0.994	0.914	1.570
Biomass cost (\$/gal)	0.823	1.091	0.766	1.066	1.069	1.174	1.133	0.955
Energy cost (\$/gal)	0.305	0.464	0.337	0.311	0.367	0.369	0.595	0.369

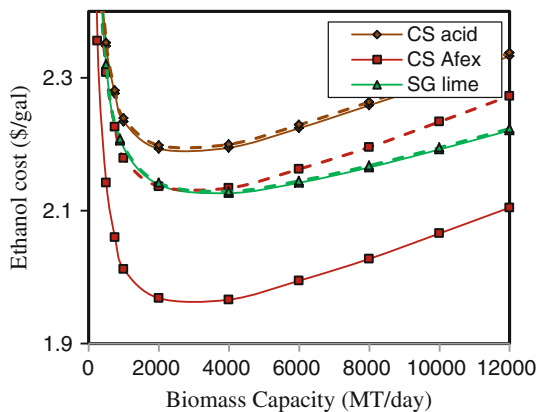
AFEX ammonia fiber explosion pretreatment, Lime Lime pretreatment, Acid Acid pretreatment, LHW liquid hot water pretreatment



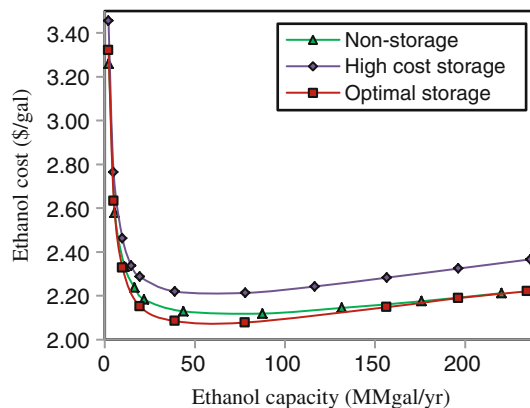
**Fig. 9** Enzyme loading variance for AFEX pretreated corn stover



**Fig. 11** Effect of storage on ethanol cost



**Fig. 10** Effect of chemical cost on ethanol price



**Fig. 12** Optimal storage for minimal ethanol cost

The conditions for which storage is always superior to non-storage would be a function of the decomposition rate and cost of storage. In reality the cost of storage would be a function of the decomposition rate since the purpose of storage would be to insure minimal feedstock loss. It was determined that the only conditions that insure the superiority of the storage scheme is with a biomass decomposition rate of 0.5 % loss/month while storage in an open field. The results for these conditions are illustrated in Fig. 12.

## Conclusion

This study focused on process synthesis, optimization, and economic evaluation of a typical bioethanol production facility. Eight different processing schemes were synthesized to account for the various biomass and pretreatment choices. By conducting computer-aided simulations using ASPEN PLUS<sup>®</sup> and utilizing nonlinear regression techniques, an optimization model in LINGO<sup>®</sup> was developed and solved for the optimal processing scheme. The results from the study indicate that the best processing option incorporates corn stover as the biomass feedstock and utilizing an AFEX pretreatment processing step. For this optimal pathway the minimal ethanol production price was determined as \$1.96/gal. This ethanol price corresponded to an optimal plant capacity of 2,788 MT/day biomass. Results also show that the optimal plant capacity for other configurations typically lay within the range of 2,000–4,000 MT/day. Chemical sensitivity analysis indicates that the AFEX pretreatment process can result in high variations in minimal ethanol price due to high fluctuations in ammonia costs. The seasonal variation model indicates that storage of biomass with a simultaneous reduction in plant capacity is a more economical approach to producing bioethanol in areas that lack sufficient biomass availability. Results also illustrate that storage schemes should be limited to plant capacities of 3,750 MT/day above which non-storage is more economical. Based on assumed conditions and cost of storage, the optimal scenario for any storage scheme requires a biomass decomposition rate of 0.5 %/month while stored open to the atmosphere.

## References

- Aden A, M Ruth et al. (2002). Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover, National Renewable Energy Laboratory, NREL/TP-510-32438
- Alizadeh H, Teymouri F et al (2005) Pretreatment of switchgrass by ammonia fiber explosion (AFEX). *Appl Biochem Biotechnol* 124(1):1133–1141
- Basu P (2010) Biomass gasification and pyrolysis: practical design and theory. MA Academic Press, Burlington
- Cardona CA, Sánchez ÓJ (2007) Fuel ethanol production: process design trends and integration opportunities. *Bioresour Technol* 98(12):2415–2457
- Cardona CA, Sanchez OJ et al (2010) Process synthesis for fuel ethanol production. CRC, Boca Raton
- Chang VS, Burr B et al (1997) Lime pretreatment of switchgrass. *Appl Biochem Biotechnol* 63–5:3–19
- Chouinard-Dussault P, Bradt L et al (2011) Incorporation of process integration into life cycle analysis for the production of biofuels. *Clean Technol Environ Policy* 13(5):673–685
- Clark JH, Deswarte FI (2008) Introduction to chemicals from biomass. Wiley, New York
- Conde-Mejía C, Jiménez-Gutiérrez A et al (2012) A comparison of pretreatment methods for bioethanol production from lignocellulosic materials. *Process Saf Environ Prot* 90(3):189–202
- Dien BS, Moniruzzaman M et al (1997) Fermentation of corn fibre sugars by an engineered xylose utilizing *Saccharomyces* yeast strain. *World J Microbiol Biotechnol* 13(3):341–346
- El-Halwagi MM (2012) Sustainable design through process integration: fundamentals and applications to industrial pollution prevention, resource conservation, and profitability enhancement. Butterworth Heinemann, Oxford
- El-Halwagi AM, Rosas C, Ponce-Ortega JM, Jiménez-Gutiérrez A, Mannan MS, El-Halwagi MM (2013) Multi-objective optimization of biorefineries with economic and safety objectives”, *AIChE J.* (in press)
- Esteghlalian A, Hashimoto AG et al (1998) Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Bioresour Technol* 59(2–3):129–136
- Farrell A, Plevin R et al (2006) Ethanol can contribute to energy and environmental goals. *Science* 311(5760):506–508
- Gwehenberger G, Narodoslawsky M et al (2007) Ecology of scale versus economy of scale for bioethanol production. *Biofuels Bioprod Biorefin* 1(4):264–269
- Honnery D, Garnier G et al (2013) Biorefinery design from an earth systems perspective. In: Stuart P, El-Halwagi MM (eds) *Integrated biorefineries: design, analysis, and optimization*. CRC, Boca Raton, pp 771–792
- Huang H-J, Ramaswamy S et al (2009) Effect of biomass species and plant size on cellulosic ethanol: a comparative process and economic analysis. *Biomass Bioenergy* 33(2):234–246
- Kamm B, Gruber PR et al (2006) *Biorefineries-industrial processes and production: status quo and future directions*. Wiley–VCH, Weinheim
- Kazi FK, Fortman J et al. (2010) Techno-economic analysis of biochemical scenarios for production of cellulosic ethanol, National Renewable Energy Laboratory, NREL/TP-6A2-46588
- Kim S, Holtzapfle MT (2005) Lime pretreatment and enzymatic hydrolysis of corn stover. *Bioresour Technol* 96(18):1994–2006
- Kim TH, Kim JS et al (2003) Pretreatment of corn stover by aqueous ammonia. *Bioresour Technol* 90(1):39–47
- Mani S, Tabil LG et al (2004) Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass Bioenergy* 27(4):339–352
- Martín M, Grossmann IE (2010) Superstructure optimization of lignocellulosic bioethanol plants. In: Pierucci S, Ferraris GB (eds) *Computer aided chemical engineering*, 28th edn. Elsevier, Amsterdam, pp 943–948
- Martín M, Grossmann IE (2011) Energy optimization of bioethanol production via gasification of switchgrass. *AIChE J* 57(12):3408–3428
- Martín M, Grossmann IE (2012) Energy optimization of bioethanol production via hydrolysis of switchgrass. *AIChE J* 58(5):1538–1549

- Mosier N, Hendrickson R et al (2005) Optimization of pH controlled liquid hot water pretreatment of corn stover. *Bioresour Technol* 96(18):1986–1993
- Ojeda KA, Sánchez EL et al (2010) Application of computer-aided process engineering and exergy analysis to evaluate different routes of biofuels production from lignocellulosic biomass. *Ind Eng Chem Res* 50(5):2768–2772
- Ojeda K, Sánchez E et al (2011) Exergy analysis and process integration of bioethanol production from acid pre-treated biomass: comparison of SHF, SSF and SSCF pathways. *Chem Eng J* 176–177:195–201
- Peters M, Timmerhaus KD et al (2003) *Plant design and economics for chemical engineers*. McGraw-Hill, New York
- Pham V, El-Halwagi M (2012) Process synthesis and optimization of biorefinery configurations. *AIChE J* 58(4):1212–1221
- Sanaei S, Janssen M et al (2013) LCA-based environmental evaluation of biorefinery projects. In: Stuart P, El-Halwagi MM (eds) *Integrated biorefineries: design, analysis, and optimization*. CRC, Boca Raton, pp 793–817
- Schrage L (2006) *Optimization modeling with LINGO*, 6th edn. LINDO Systems, Chicago
- Sissine F (2007) CRS Report for Congress. Energy Independence and Security Act of 2007. [http://energy.senate.gov/public/\\_files/RL342941.pdf](http://energy.senate.gov/public/_files/RL342941.pdf). Accessed 28 Oct 2011
- Steele B, Raj S et al (2005) Enzyme recovery and recycling following hydrolysis of ammonia fiber explosion-treated corn stover. *Appl Biochem Biotechnol* 124(1):901–910
- Stuart P, El-Halwagi MM (2013) *Integrated biorefineries: design, analysis, and optimization*, CRC, Boca Raton
- Teymouri F, Laureano-Perez L et al (2005) Optimization of the ammonia fiber explosion (AFEX) treatment parameters for enzymatic hydrolysis of corn stover. *Bioresour Technol* 96(18):2014–2018
- Wenzel H (2009) Biofuels: the good, the bad, the ugly - and the unwise policy. *Clean Technol Environ Policy* 11(2):143–145
- William E, Johanns A et al. (2011) Cash Rentals Rates for Iowa. <http://www.extension.iastate.edu/agdm/wholefarm/pdf/c2-10.pdf>. Accessed 28 Oct 2011