

Energy, sugar dilution, and economic analysis of hot water flow-through pre-treatment for producing biofuel from sugarcane residues

Véronique Archambault-Léger, Dartmouth College, Thayer School of Engineering, Hanover, NH Zachary Losordo, Mascoma Corporation, Modeling, Lebanon, NH Lee R. Lynd, Dartmouth College, Thayer School of Engineering, Hanover, NH

Received May 28, 2014; revised August 2, 2014; accepted September 17, 2014 View online at Wiley Online Library (wileyonlinelibrary.com); DOI: 10.1002/bbb.1524; *Biofuels, Bioprod. Bioref.* (2014)

Abstract: Hot water flow-through (FT) pre-treatment of cellulosic biomass for biofuel production offers key performance advantages over other pre-treatment methods. The present study aims to address the energy demand, sugar dilution, and economic concerns of using FT pre-treatment for the bioconversion of sugarcane bagasse and trash to ethanol. FT pre-treatment resulted in a lower minimum ethanol selling price (\$0.82/L) than dilute acid (\$1.01-1.19/L), hot water (\$1.13-1.27/L) and steam explosion (\$0.86–1.18/L) (the range represents different studies). Sugar dilution was not a limiting factor provided that extensive heat integration was employed, as is the case in an oil refinery. The ethanol beer to distillation contained 5.0 wt% ethanol. Integrated first-generation and second-generation plants with no external fuel supplied were examined based on conversion of sucrose, bagasse, and available cane trash. A base case was defined using FT pre-treatment which routed all of the bagasse and 31.8% of the trash to ethanol production. For an alternative 'best parameter' case, all of the bagasse and available trash was routed to ethanol production, leaving 1.1% of the feedstock higher heating value available for electricity exports. Ethanol yields for the base case, best parameter case and steam explosion case were 59.9, 81.6, and 50.8 L/wet ton cane respectively, representing increases of 79%, 108%, and 67% compared to the first-generation plant. Our results indicate that sugar dilution and energy consumption are not barriers to practical commercial implementation of flow-through pre-treatment, and that FT pre-treatment has potential to be economically advantageous compared to hydrothermal and dilute acid pre-treatments. © 2014 Society of Chemical Industry and John Wiley & Sons, Ltd

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

Keywords: technoeconomic; sugarcane bagasse; pre-treatment, flow-through; biofuel; energy

Correspondence to: Lee R. Lynd, Dartmouth College, Thayer School of Engineering, 14 Engineering Drive, Hanover, NH, 03755. E-mail: Lee.R.Lynd@dartmouth.edu

Introduction

roducing fuel from lignocellulosic biomass is of interest in the context of developing a sustainable global energy system, with key potential benefits including climate change mitigation and economic development.¹ Sugarcane residues such as bagasse, pre-collected at sites with substantial existing infrastructure, are widely seen as a particularly promising resource for initial commercial application.^{2,3} Sugar and ethanol production from sugarcane is a major industry with important contributions to agriculture, economic development, and social well-being in several countries, in particular Brazil.^{4,5} Modern plants achieve fossil fuel displacement ratios (displaced fossil fuel:fossil fuel use across the supply chain of 10:1) and correspondingly large greenhouse emission reduction.^{4,5} Boosting ethanol production using lignocellulosic sugarcane residues, such as bagasse and cane trash, would provide further fossil fuel displacement.

Processing bagasse using commercially available cellulases requires pre-treatment to obtain high biofuel yield. Prior work indicates that hot water flow-through (FT) pre-treatment typically achieves higher solids reactivity, higher hemicellulose removal, less sugar degradation, and substantially higher removal of lignin compared to pre-treatment in non-FT configurations at the same temperature and residence time.⁶⁻¹² Practical operation of FT pre-treatment is challenging because of the complexity of arranging a biomass reactor in an FT mode at reaction temperature and pressure, and because of higher water usage compared to non-flow configuration.⁶ In lignocellulose processing, high carbohydrate concentrations, and hence high solids concentrations, are desirable in order to have high concentrations of ethanol for fermentation and separation operations. As the concentrations of solids, carbohydrate, and ethanol are reduced, economic and energetic penalties become progressively steeper, particularly below 4 wt. % ethanol using conventional distillation.¹³ At the same time, solids handling and mixing issues become more difficult at high solids concentrations, and as a result ethanol concentrations in designs for lignocellulose processing with conventional pre-treatment seldom exceed 6 wt. %.^{14,15} Low solids concentrations, and the high extent carbohydrate and hence ethanol dilution that accompany them, are more challenging to avoid for FT pre-treatment than for non-FT configurations, and have often been cited as a factor constraining practical application.^{6,16} Integrated processing of the juice and fiber fractions of sugarcane to ethanol may offer an added degree of freedom, at least for new plants, because of the possibility

of mixing ethanol-containing broth from lignocellulose processing with that from processing cane juice.

In prior work, we found that FT pre-treatment of sugarcane bagasse becomes mechanically infeasible when the solids concentration entering the pre-treatment reactor exceeds 140 kg/m³, but appears to be possible at solids concentration of 140 kg/m³ or less.¹⁷ Several configurations have been proposed and investigated to address the water usage and energy consumption concerns including 'recirculation flow', 'counter-current flow', and 'partial flow'. Recirculation mitigates dilution and energy consumption but has a negative impact on pre-treatment performance.⁶ Counter-current flow could produce a higher concentration of solubilized sugar and less sugar degradation as compared to more conventional configurations, but is the most challenging to implement.¹⁸ Partial flow, where the pre-treatment reactor includes sections of FT and sections of plug flow, was shown to increase hemicellulose and lignin removal and to yield more reactive fibers compared to batch operation.¹⁶ Simulated performance of several pre-treatment configurations showed that partial flow could provide highly digestible solid fibers and sugar recovery nearly as high as a complete countercurrent configuration while being considerably simpler to implement.19

Technoeconomic studies based on updated models developed at the National Renewable Energy Laboratory^{20,21} have evaluated pre-treatment using dilute acid, hot water, and steam explosion. Both Kazi *et al.*²² and Kumar *et al.*²³ found that capital and operating costs are lower for steam explosion and hot water pre-treatment as compared to pretreatment using dilute acid. These studies rank pre-treatment process differently with respect to economic attractiveness, and the differences are attributable in significant part to different overall ethanol yields as follows: dilute acid (288.8 L/dry ton corn stover,²² 252.6 L/dry ton grass straw²³), hot water (215.8 L/dry ton corn stover,²² 255.3 L/ dry ton grass straw²³) and steam explosion (230.2 L/dry ton grass straw²³). No techno-economic analysis has yet evaluated the economics of FT hot water pre-treatment.

The present study was undertaken to: (i) define the feasible domain for FT pre-treatment in terms of solids concentration, temperature, and process configuration for integrated processing of sucrose, bagasse, and available cane trash (assumed to be 50% of total trash),²⁴ and (ii) compare the calculated minimum ethanol selling price (MESP) for FT pre-treatment to that for other pre-treatment configurations. The study emphasizes comparing technologies rather than the US and Brazilian situation, making internally consistent cost assumptions about the process with two different sets of parameters for feedstock and product prices.

Process description

Base case scenario

A base case scenario was defined representing, to the best of the authors' knowledge, a biorefinery which could be expected if built today according to current practices. A Brazilian sugarcane processing facility processing 1300 dry tons/day of bagasse and 700 dry tons/day of trash for 200 days/year was assumed following Dias et al.²⁴ The composition of both bagasse and trash, which can vary significantly depending on the sample,^{25,26} was assumed to be 43% cellulose, 23% lignin, 26% xylan, 4% acetate, and 4% ash.²⁴ A flow diagram is shown in Fig. 1. Pre-heated water is mixed with the biomass from the sugar mill, to which steam is then injected to heat the slurry to the desired temperature of 210°C. The performance of FT pretreatment is based on prior studies of kinetics¹⁹ and fluid mechanics.¹⁷ During FT pre-treatment at 210°C, 95% of xylan is converted to xylose and xylo-oligomers, 4.5% of xylose is converted to degradation products, 50% of lignin is solubilized.

Following pre-treatment, the washate, containing the solubilized compounds, is sent through a counter-current heat exchanger to pre-heat the pre-treatment inlet water and then through multi-stage evaporation to 20 kPa. The solids are flashed from 50% to 43% moisture and the resulting steam is sent to help drive distillation along with the steam from the multi-stage evaporator. The flashed

solids are mixed with enzymes, nutrients, and treated recycled water as required for the cellulose fermentation broth to contain 6.0+/-0.1% ethanol. Nutrients and enzymes are also added to the concentrated hemicellulose stream from the multi-stage evaporator and fermented. It was assumed, based on NREL's study,²² that 7% of all fermenting sugars were lost to contamination. Heat integration, using the hot washate to pre-heat inlet water and the steam from the flashed solids and multi-stage evaporator, is very important to drive down the energy consumption of the process, particularly for distillation.

The cellulose and hemicellulose ethanol streams are combined, pre-heated with the distillation bottoms, de-aired to remove carbon dioxide and sent to distillation. The reflux ratio and reboiler duty are set to generate 94 +/- 1wt% and 0.01 +/- 0.005wt% ethanol at the top and bottom of the distillation column, respectively. The treatment of the residues from the distillation bottoms is illustrated in Fig. 2. They are sent to waste water treatment, where soluble carbohydrate residues are anaerobically digested with an assumed extent of reaction of 97%. Then, the remaining solids are centrifuged to 47% solids. The liquid containing 2% soluble lignin is evaporated to a 64% concentration and burned. The solids are further dried to 60% solids by open heat exchange with the combustor flue gases. The flue gases are then used to preheat the air inlet to the combustor. It was assumed that all of the lignin can be burned.

Thermodynamic calculations, including calculating the combustor efficiency, were performed using higher heating values (HHV) as reported in Table 1.



Figure 1. Flow diagram illustrating the base case process for sugarcane residues biological conversion to ethanol.



Figure 2. Flow diagram illustrating the treatment of the distillation bottoms in the base case scenario, evaporating soluble lignin to a concentrated syrup.

Table 1. Main materials higher heating values (MJ/kg).									
	Bagasse and trash	Ethanol	Lignin	Cellulose	Xylan	Methane	Biomass	Acetate	
HHV (MJ/kg)	19	29.7	26.7	17.3	17.8	55.5	22.9	7	



Figure 3. Flow diagram illustrating the sugarcane residues biological conversion to ethanol using steam explosion pre-treatment.

When there is more energy left over from residue processing than is required for both the second-generation plant (making ethanol from bagasse and trash) and the first generation plant (making sugar from cane juice), the energy can be exported as electricity. This electricity export is accounted for as by-product (electricity) credits at the Brazilian price of \$0.085 / kWh.²⁴

Comparison with steam explosion

FT pre-treatment as described above was compared to a process using steam explosion, shown in Fig. 3. Steam explosion pre-treatment at 190°C for 15 min solubilizes about 90% of the hemicellulose and 10% of the lignin and cellulose.²⁸ 13% of the solubilized hemicellulose¹⁹ and 50%

Table 2. Process parameters sensitivity values.			
	Low	Base case	High
Pre-treatment temperature (°C)	170	210	-
Hemicellulose degradation	2	4.5	7
Liquid:Solids mass ratio (in the center of the pre-treatment reactor)	4.5	6	7.5
Ethanol concentration from cellulose stream	-	6	10
Compressor drive	Direct steam turbine	Electrical	-
Use of IHOSR distillation	Yes	No	-
Residue processing scenario	Biomethanation of soluble lignin	Evaporate and burn soluble lignin	-
Fermentation strategy	-	Separate	Combined

of the solubilized cellulose are degraded.²⁹ The pre-treated solids are washed with 3:1 water:solids at 90°C which removes 95+/–2% of the soluble compounds (hemicellulose, lignin, furfural, HMF, acetic acid, and glucose) from the cellulose fibers. Using no detoxification, 75 % of the solubilized hemicellulose is converted to ethanol during fermentation³⁰ and 90% of the cellulose is converted to ethanol.¹⁹

Sensitivity analysis

Parameters were varied to study the effect on energy consumption and economics. The varied process parameters along with their low, base case and high values are listed in Table 2. A fermentation strategy was considered where the hemicellulose liquid stream was used to dilute the cellulose stream resulting in a combined instead of separate fermentation. The ethanol concentration resulting from the combined fermentation was 9.1%. Both the steam explosion and FT pre-treatment configurations were analyzed with base-case parameter values, while the sensitivity analysis was performed on the FT pre-treatment process.

Motivated by a desire to minimize steam consumption, the use of distillation with intermediate heat pumps and optimal sidestream return (IHOSR) was evaluated.²⁷ The IHOSR configuration used here involves removal of some of the vapor at point of feed introduction, compressing it, condensing it in the reboiler so that vapor is generated at the bottom of the column, and returning the condensed ethanol-water mixture at the point in the column where the liquid composition is close to that of the returned stream. It may be noted that the return stream is typically enriched in ethanol by about 5.5-fold on a mole basis compared to the fermentation broth, and that use of heat pumps in this configuration is more efficient than compressing the overhead vapor.²⁷ The compressors in IHOSR and in the multi-stage evaporator were electrically driven, but the impact of steam drive was evaluated.

The base case scenario considered a residue processing method where soluble lignin was evaporated and concentrated to a 64% lignin syrup and burned as illustrated in Fig. 2. An alternative residue processing scenario was considered, illustrated in Fig. 4, where the soluble lignin was anaerobically digested to methane along with the carbohydrates. Although commercial application of anaerobic digestion of lignin derivatives has not yet been developed, there is strong scientific evidence that lignin oligomers can undergo near complete anaerobic depolymerization and that lignin monomers can be completely metabolized anaerobically.^{31,32} In both the base case and best parameter scenarios, the soluble carbohydrate residues were anaerobically digested.

The impact on the minimum ethanol selling price (MESP) was studied for the liquid-to-solids mass ratio, the ethanol concentration from the cellulose stream, the compressor drive, the use of IHOSR distillation, the residue processing scenario and the fermentation strategy (last 6 rows in Table 2). Variation in equipment size was evaluated using the exponential scaling expression given by Aden *et al.*,²¹ and the addition or removal of equipment were evaluated using the Icarus software in Aspen plus.

A best parameter scenario was evaluated using parameters that are favorable to high yield and low MESP. The differences between the base case and best parameter scenario are summarized in Table 3.

Results and discussion

Heat integration and dilution minimization

In light of the desirability of minimizing dilution of process streams with water, our design for FT pre-treatment featured heat integration wherever possible. Thus the wash



Figure 4. Schematic illustrating the treatment of the distillation bottoms in the best parameter scenario, using anaerobic digestion of soluble lignin.

Table 3. Process parameters for base caseversus best parameter case.								
	Base case	Best parameter case						
Pre-treatment temperature (°C)	210	190						
Use of IHOSR	No	Yes						
Soluble lignin process- ing scenario	Evaporate and burn	Biomethanation						
Fermentation strategy	Separate	Combined						

water to pre-treatment was heated to 90°C by exchange with liquid from the multi-stages evaporator, and further pre-heated by counter-current heat exchange with the washate from pre-treatment to 15°C below the pre-treatment temperature, corresponding to 195°C for the base case scenario. Thirty-nine percent of the solid compounds are solubilized and washed away during pre-treatment leading to a higher volume of washate in the counter-current heat exchanger compared to the water volume to be pre-heated. This feature results in the washate cooling to 135°C through the heat exchange, retaining enough energy for efficient multi-stage vacuum flashing without additional energy input. Indeed, flashing the cooled washate to 20 kPa removes 20% of the stream mass as steam. The energy in the steam can be recovered via a heat exchanger to complement the reboiler heat duty. Furthermore, flashing removes 44% of the furfural and 9% of the acetic acid from the hemicellulose stream. The resulting hemicellulose stream to fermentation contains 65 g/L hemicelluloses, which is not too dilute and not expected to be inhibited by the low level of furfural $(1.5 \text{ g/L})^{33,34}$ and

acetic acid (4.2 g/L) if the pH is controlled.³⁵ This stream can be fermented to 2.9% ethanol, but when combined with the cellulose ethanol stream the combined beer sent to distillation contains 5.0% ethanol, which is a satisfactory pre-distillation concentration. Thus, using heat integration strategies and flashing to remove excess water as usable steam allows sufficient concentration of the sugar streams, addressing one of the primary concerns relative to FT pre-treatment.

Energy consumption

First-generation energy consumption calculation

Parameters for cane juice processing were taken from previous studies as listed in Table 4. It was concluded that 28.6% of the bagasse and trash HHV must be utilized to run an advanced sugar mill with 50% cane trash processing.

Comparison with steam explosion

Figure 5 illustrates that of the energy available from bagasse and trash, 10% more is lost to combustor inefficiency using steam explosion than the base case FT pretreatment. This difference results from the greater amount of residues after steam explosion leading to more residues being burnt compared to FT pre-treatment.

It is important to note that the heat integration described in the process description, including counter-current heat exchange, solids flashing, and multi-stages evaporator to vacuum, allows reuse of all pre-treatment steam in distillation. The energy from the pre-treatment steam used

Table 4.	Charact	eristics	of the mo	dern mill.

Parameter	Value
Milling capacity	10 wet kton/day
Operating days	200
Bagasse and trash availability	130 and 70 kg/wet ton sugarcane, respectively ²⁴
Bagasse and trash higher heating value (HHV)	19 MJ/kg ³⁶
Boiler efficiency	0.787 ³⁷
Electricity generation efficiency	0.65
Steam demand	260 kg/ton wet cane ^{38,39}
Electricity demand	28 kWh/ton ³⁹
Steam enthalpy	2700 kJ/kg
Energy available/ton wet cane ^a	2991 MJ/ton
Process energy demand ^b	857 MJ/ton
Surplus energy	2134 MJ/ton
% of bagasse and trash required for process ^c	28.6
^a (mass of bagasse+trash available) x b boiler efficiency.	pagasse and trash HHV x

^bSteam demand x steam enthalpy + Electricity demand / generation efficiency.

^cProcess energy demand / Energy available.

to preheat the inlet streams is recovered by flashing the washate to vacuum and the pre-treated solids. The steam generated is directly injected at the bottom of the distillation column, which supplies 82% of the distillation energy demand.

With regard to sugarcane residues HHV, 33.3% and 46.0% can be converted to ethanol using the base case and best parameter case FT pre-treatment, respectively, compared to 31.4% for steam explosion, as illustrated in Fig. 5. This difference is due to the greater degradation of

carbohydrates during steam explosion pre-treatment as well as the highly reactive FT pre-treated carbohydrates (67% and 57% of theoretical yield for FT pre-treatment and steam explosion). The lower steam addition required to heat up the pre-treatment process and the greater amount of residuals using steam explosion compared to the base case results in more of the bagasse and available trash used for ethanol processing (94.6%) compared to the base case (76.1%).

Energy sensitivity analysis

The residual solids and pre-treatment scenarios described above have a largest impact on the energy balance of the combined first and second generation plant, as shown in Fig. 6. Anaerobically metabolizing soluble lignin to methane is highly desirable from an energetic perspective. It decreases the amount of trash to be burned to supply all the energy for the combined first- and second-generation processes by 30.1%.

The pre-treatment temperature has the next largest impact, and decreasing it from 210 °C to 170 °C decreases the amount of trash to be burned by 24.0%. Omitting the use of IHOSR would increase energy demand and increase the amount of trash to be burned by 17.9% to supplement the second-generation plant energy needs. Combining the hemicellulose and glucose fermentation by diluting the solids with the washate would decrease the amount of trash to be burned by 5.1%. All other process parameters studied, including the nature of the compressor drive, the ethanol concentration from the glucose stream, the liquid to solids mass ratio during pre-treatment and the hemicellulose degradation had an effect of less than 5% on the amount of trash to be burned or the amount of feedstock HHV left-over to sell as electricity credits.



Figure 5. Trash and bagasse energy (HHV) breakdown.



Figure 6. Process parameters sensitivity on the variation of trash % to be burned to maintain energy self-sufficiency.

Summary

The primary goal of the energy analysis was to determine whether a second-generation plant could be integrated with a first-generation plant, with all process energy derived from process residues. In the base case, 68.2% of the trash would need to be burned without first being converted to ethanol. Using parameters favorable to high yield, all the available trash and bagasse could be processed to ethanol, leaving 1% of the bagasse and trash HHV as energy surplus, as was illustrated in the best parameter scenario.

Economic analysis

The economics of using FT pre-treatment to biologically convert 2000 tons of bagasse and trash per day to ethanol were analyzed by comparing to two previous studies by Kazi et al. at NREL²² and by Kumar and Murthy at Oregon State University.²³ NREL's study uses corn stover as a model feedstock and analyzes several pre-treatments including dilute acid and hot water. Kumar's study uses tall Fescue and also analyzes several pre-treatments including dilute acid, steam explosion, and hot water. Both studies are full bottom-up analysis. Here, the differences incurred by using FT instead of dilute acid, steam explosion or hot water are analyzed along with their economic impacts. All economic assumptions are the same as in the NREL study except that the bagasse and trash plants operate for 200 days per year compared to 350 for corn stover. All costs were scaled to 2013 dollars using the chemical engineering price index.⁴⁰ Kumar's results were scaled to

process 2000 tons of grass per day. Since feedstock cost is typically the largest driver of ethanol production cost⁴¹ and since bagasse is cheaper than corn stover and tall Fescue, all feedstock costs were scaled to \$55/ton and 350 operating days per year to focus the comparison on the pre-treatment method.

Capital cost

Table 5 describes the main areas affected by the choice of pre-treatment (left column), how these areas are affected (middle columns) and the impact on the overall cost of biological conversion (right column). The FT pre-treatment reactor is more complex because it must include four screw feeders, a system of screens, piping and valves, which we estimate would add about \$18M.42 Although this number is speculative at this point, it is small enough that the impact of it varying by 1-fold is relatively small (a \$0.012 MESP increase) and would not significantly change the conclusions herein. A continuous bagasse reactor is more expensive than a wood, corn stover, or grass reactor because the flowability characteristic of bagasse indicates that an auger should be used in the reactor to ensure stable continuous flow without plugging. This adds another \$7M to the pre-treatment reactor, as calculated by the Aspen Plus Icarus software. The FT reactor also needs to be larger because the solids concentration must be lower (140kg/m^3) than LHW (17%) and steam explosion (50%). Following the exponential scaling expression given by Aden et al.,²¹ the FT reactor is expected to be 11% more expensive than the LHW reactor and 2.16 times more expensive than the

Table 5. Economic impacts of FT pre-treatment with sugarcane bagasse on biological conversion of sugarcane bagasse and trash to ethanol.

	Features	Details	Cost impact
Pre-treatment Reactor	Auger, screw feeder system	Calculated from icarus software (Aspen Plus)	Add \$7.6M to hot water and steam explosion reactors.
	Screen, piping and valve system for FT operation		Add \$3M for 1252 L/dry kg capacity ⁴²
	Solids loading	FT : 14w/v% Steam explosion: 50w/v% Liquid hot water 17 w/v% ²²	FT cost = steamX cost * (3.6)^0.6 ²² FT cost = LHW cost * (1.2)^0.6 ²²
	Additional screw feeders, pump, CC heat exchanger and multi-stages vacuum evaporator	Calculated from icarus software (Aspen Plus)	Pump: \$110,000 Heat exchanger: \$450,000 Multi-stages vacuum evaporator: \$1M Four screw feeders: 15M
Effect of FT on operations other than	Compared to steam explosion	FT has no need for detoxification and post- pre-treatment washing.	
pre-treatment	Compared to hot water	FT has no need for detoxification and post- pre-treatment washing. Lower dist \$ because beer concentration is 5.8% for FT analysis vs. 2.7% for NREL hot water. WWT in the present study includes soluble lignin (50% of original lignin).	\$9.1M less in fermentation FT dist \$ = HW dist \$* (2.7/5.8)^0.33 \$1.9M more in waste water treatment
	Compared to dilute acid	FT has no need for detoxification, post- pre-treatment washing, solvent recovery and recycling. Lower dist \$ because beer concentration is 5.8% for FT analysis vs. 4.7% for NREL dilute acid.	\$21.6M less in pre-treatment area FT dist \$ = DA dist \$* (4.7/5.8)^0.33
Effect of feedstock on upstream operations	Compared to corn stover	Collecting and handling bagasse already done in existing 1G plant. Trash cost assumed same as corn stover.	\$7.2M less in feedstock handling area
	Compared to grass	Crushing already done in sugar mill	
Raw material	Feedstock price	Corn stover: \$83/ton ²² Grass straw: \$50/ton ²³ Sugarcane bagasse and trash: \$23/ton*	\$48.7M/yr lower operating expense using bagasse for 200 days/yr at \$23/ ton compared to NREL's corn stover at \$83/ton for 350 days/yr
	Water	14 kton/day more water at \$0.4/ton	\$1.1M/yr more for water compared to hot water
	Cellulase, hemicel- lulose and Corn Steep Liquor (CSL)	NREL assumed 35.1 mg/g cellulose Scaled according to mass of fermentable sugars to fermentation; FT has less cellulose but more xylo- oligomers to fermentation compared to DA	\$0.8M less cellulase and hemicellu- lose, \$0.2M less CSL
	Others	Less compared to DA Same as hot water and steam explosion	\$8.1M/yr less compared to DA
Waste disposal		Less compared to DA Same as hot water and steam explosion	\$5.8M/yr less compared to DA
Ethanol Yield	Steam explosion: 238.5 L/dry ton (3% higher than ²³) FT liquid hot water: 375.4 L/dry ton	Ethanol selling price: 0.5\$/L Electricity price: \$0.085/kWh in Brazil ²⁴ 15.3% more of the feedstock HHV can be used as electricity credit with steam explosion compared to FT.	$ \begin{array}{l} \mbox{Higher ethanol revenues with FT:} \\ R_{ethanol} = \$24.5 \mbox{M/yr greater for FT} \\ R_{electricity credit} = \$7.2 \mbox{M/yr lower for FT} \\ R_{FT} - R_{steam explosion} = \$17.3 \mbox{M/yr} \end{array} $

* Bagasse and trash cost about \$10³⁷-26⁴⁴ and \$13³⁷-17²⁴/ton, respectively. Here, a high-end cost for bagasse and trash were assumed (weighed for the amount available), corresponding to \$23/ton of second-generation feedstock.

Table 6. Economic comparison between present study, NREL, ²² and Kumar and Murthy ²³ (2013 dollars).											
	NREL (corn stov		rn stover)	over) ^a Present study tra		y (bagasse and ash)		Kumar and Murthy		(grass) ^a	
	dilute acid hot		hot w	ater FT base case		oase se	steam explosion		dilute acid	steam explosion	hot water
					Installed		d Cost				
Cost Areas / Factor	(M\\$)	(%)	(M\\$)	(%)	(M\\$)	(%)	(M\\$)	(%)	(M\\$)	(M\\$)	(M\\$)
Feedstock Handling ^b	11.8	6.4	11.8	7.0	4.6	0.3	4.6	3.1			
Pre-treatment	41.0	22.4	7.2	4.3	29.9	18.4	3.8	2.5			
Saccharification & Fermentation	23.5	12.9	32.6	19.3	23.5	14.4	32.6	21.8			
Distillation and Solids Recovery ^c	27.7	15.1	33.4	19.8	27.8	17.1	33.4	22.3			
Wastewater Treatment	6.3	3.4	2.1	1.2	4.0	2.5	2.1	1.4			
Storage	3.3	1.8	3.6	2.1	3.6	2.2	3.6	2.4			
Boiler/Turbogenerator	62.2	24.4	71.0	42.1	62.2	38.2	62.2	41.6			
Utilities	7.1	3.9	7.2	4.3	7.2	4.4	7.1	4.8			
Total Installed Equipment Cost	182.9	100	168.765	100	162.9	97	149.3	100	165.2	131.6	146.8
Fixed Capital Investment (FCI)	364.7		339.0		325.8		298.7		330.3	263.3	293.6
Working Capital (WC)	54.7		50.9		48.9		44.8		49.6	39.5	44.0
Total Capital Investment (TCI)	418.9		389.9		374.7		343.5		379.9	302.8	337.7
Operating costs (M\$/yr)											
Feedstock (constant)	38.5		38.5		38.5		38.5		38.5	38.5	38.5
Feddstock (differnet)	62.5		62.5		9.2		9.2		35	35	35
CSL	9.2		12.0		9.0		6.6				
Cellulase and hemicellulase	40.1		40.1		39.3		28.7				
Other Raw Matl. Costs	10.3		2.2		3.3		2.2				
Waste Disposal	7.3		1.5		1.5		1.5				
Electricity ^e	-12.6		-12.2		0		-1.8				
Fixed Costs	10.7		10.4		9.7		8.7				
Capital Depreciation	17.6		17.0		15.7		14.1				
Average Income Tax	18.0		17.1		13.1		12.9				
Sum (constant feedstock)	139.0		126.4		130.2		114.4		154.4	142.1	148.3
Sum (different feedstock)	163.0		150.4		100.9		82.1		150.9	138.6	144.8
Cost analysis summary											
Product Value (\$/L) ^d	1.01		1.27		0.82		0.86		\$1.19	\$1.18	\$1.13
Ethanol production (MML/Year)	202.2		147.6		223.7		191.7		179.634	161.1	178.7
Ethanol yield (actual/theoretical)	65%		47%		72%		61%		57%	51%	57%
Feedstock (dry metric ton/year)	700000		700000		700000		700000		700000	700000	700000
Ethanol Yield (L / Dry Metric Ton Feedstock)	288.8		210.8		319.6		273.8		256.6	230.2	255.3
Ethanol Yield (L / Wet Ton Cane)					63.9		54.8				
Feedstock Cost \$/Dry Metric Ton	55		55		55		55		55	55	55
Internal Rate of Return (After-Tax)	15%		15%		15%		15%		15%	15%	15%
Equity Percent of Total Investment	100%		100%		100%		100%		100%	100%	100%

^aScaled to 70MT of biomass processing.

^bWhen integrating with 1G plant.

^cSize factor using exponent = 0.33.

^dCalculated using discounted cash flow =\$0 after 20 years at 15% IRR.

^eElectricity credits in other studies are based on leftover after 2G use, credits in the present study are based on leftover after combined 1G and 2G use. This is not a fair comparison but even so bagasse economics are more favorable.

steam explosion based on size. Finally, an additional heat exchanger, pump, and a multi-stages vacuum evaporator to concentrate the washate are necessary for the FT process, adding approximately \$1.56 million. However, since FT generates very little degradation products¹⁹ and does not use chemicals, several operations are not required using FT including detoxification, post pre-treatment washing, solvent recovery and recycling, reducing the costs in the pre-treatment area other than the pre-treatment reactor by \$31.3 million compared to dilute acid.

Bagasse has a significant advantage over corn stover in the collecting and handling area because it is already collected and is a product of the sugar mill. Trash collection and handling is assumed here to cost the same as corn stover as derived in NREL's study,²² although the actual cost will depend on the collection strategy used.³⁷ This feature of bagasse availability reduces capital investment by \$6.9 million in the feedstock handling area. Fermentation is assumed here to cost the same using FT and dilute acid pre-treatments, because both are very effective at rendering the cellulose fibers reactive.

Adding all the equipment cost as presented in Table 6, the total capital investment is lowest for steam explosion (\$302.8 million to \$343.5 million²³), intermediate for FT (\$374.7 million) and hot water (\$337.7 million²² to \$389.9 million²³), and highest for dilute acid (\$379.9 million²² to \$418.9 million²³).

Operating costs

Waste disposal costs the same for FT, steam explosion and hot water, and is \$5.8 million/yr higher for dilute acid. Other materials cost, including water at \$0.4/ton, cost \$1.1 million/yr more for FT and \$11.1 million more for dilute acid compared to hot water and steam explosion. Average income tax for this study was calculated at the Brazilian rate of 34%, which is slightly lower than the US rate of 40%.⁴³ With 700 000 dry ton/year of feedstock processed, the total operating costs of dilute acid, hot water and FT hot water were similar (within 5% variation) and the total operating costs of steam explosion were 32-38% lower. The MESP is mostly driven by the ethanol yield which is highest for FT hot water (72% of theoretical), intermediate for dilute acid (57-65% of theoretical) and lowest for steam explosion (51-61% of theoretical). Hence, economic analysis without considering feedstock effects suggests that FT pre-treatment results in a lower MESP (0.80\$/L) compared to dilute acid (\$1.01-1.19/L) and steam explosion (\$0.86-1.18/L).

Revenues

The large differences in ethanol yield obtained using different pre-treatment results in major revenue and electricity credits differences. Actual/theoretical ethanol yields are lowest for steam explosion (51-61%) and hot water (47-57%), intermediate for dilute acid (57-65%) and highest for FT pre-treatment (72%) (Table 6). Lower ethanol yield is also associated with higher residues, which can be recovered and sold as electricity credits. However, since ethanol has a higher selling price (\$0.043/MJ at \$1.00/L MESP) than electricity (\$0.024/MJ at \$0.085/kWh), making more ethanol at the expense of electricity is advantageous. In the present study with constant feedstock, the ethanol revenues are \$22.7 million/yr greater for FT and the electricity revenues are \$1.8 million/yr greater for steam explosion, resulting in \$20.9 million/yr higher revenues for FT.

Minimum ethanol selling price

The minimum ethanol selling price (MESP) was calculated by performing a discounted cash flow analysis as described by Kazi²² using a 15% internal rate of return and



Figure 7. Effect of sensitivity parameters on MESP.

a 20-year plant life. The impact of the IRR on the MESP is illustrated in Supplemental File 1. Our analysis indicated that FT has the lowest MESP (\$0.82/L) because of its high ethanol yield, low operating costs and low capital costs in areas other than the pre-treatment reactor.

The lower ethanol yield in the NREL dilute acid study compared to the FT present study is due to 10% less cellulose in the raw feedstock (33% cellulose in corn stover vs. 43% in bagasse) and lower overall conversion of xylan to ethanol (57% for NREL dilute acid vs. 82% for present study FT).

Cost sensitivity analysis

The impact of the sensitivity parameters on the MESP is small, as shown in Fig. 7. The largest single factor was the use of combined fermentation, which decreased the MESP by \$0.02/L. The best parameter case was \$0.04/L lower than the base case.

Conclusions

Our process modeling and economic analysis indicated that sugar dilution and energy consumption are not barriers to practical commercial implementation of FT pre-treatment. Sugar dilution was not a limiting factor, as extensive heat integration can be used to pre-heat pretreatment water with minimal heat loss from the washate, which can then be flashed to remove 20% of the washate mass. The resulting ethanol beer to distillation contains 5.0% ethanol, which is not considered too dilute. Provided that extensive heat integration is used, as is the case in the oil refinery industry, it is possible to add a second-generation plant to a first-generation sugarcane plant, making ethanol from the sugarcane bagasse and trash, with all of the energy supplied from process residues and some energy left-over to sell as electricity exports. Although process assumptions made to attain this best parameter scenario may be viewed as optimistic, the base case scenario show that with conservative assumptions, burning 68.2% of the available trash would maintain energy selfsufficiency. Our analysis indicated that FT pre-treatment provided a lower ethanol selling price (\$0.82/L) than other pre-treatment methods considered (\$0.86/L-\$1.27/L). Thus, FT pre-treatment does not only yield highly reactive fibers, but it is also very promising for commercial implementation.

Acknowledgements

The authors are grateful for the support provided by funding grants from the Link Energy Foundation, the

BioEnergy Science Center (BESC), a US Department of Energy (DOE) Research Center supported by the Office of Biological and Environmental Research in the DOE Office of Science, Oak Ridge National Laboratory, and Mascoma Corporation. Oak Ridge National Laboratory is managed by University of Tennessee UT-Battelle LLC for the Department of Energy under Contract No. DE-AC05-00OR22725.

References

- 1. International Energy Agency, *Energy Technology Perspectives* 2012: Pathways to Clean Energy System. OECD Publishing, Paris, France (2012).
- Chandel AK, Giese EC, Antunes FAF, Oliveira IdS and Silva SSd, Pre-treatment of sugarcane bagasse and leaves: Unlocking the treasury of "Green Currency", in *Pre-treatment Techniques for Biofuels and Biorefineries*, ed by Fang Z. Green Energy and Technology, Springer-Verlag, Berlin Heidelberg (2013).
- 3. Canilha L, Chandel AK, Milessi TSdS, Antunes FAF, Freitas WLdC, Felipe MdGA *et al.*, Bioconversion of sugarcane biomass into ethanol: An overview about composition, pre-treatment methods, detoxification of hydrolysates, enzymatic saccharification, and ethanol fermentation. *J Biomed Biotechnol* 2012:15 (2012)
- Macedo IC, Sugar Cane's Energy: Twelve Studies on Brazilian Sugar Cane Agribusiness and Its Sustainability. UNICA - Sao Paulo Sugar Cane Agroindustry Union, São Paulo (2005).
- 5. World Watch Institute, *Biofuels for Transportation: Global Potential and Implications for Sustainable Agriculture and Energy in the 21st Century.* World Watch Institute, Washington DC (2006).
- 6. Bobleter O, Hydrothermal degradation of polymers derived from plants. *Prog Polym Sci* **19**:797–841 (1994).
- 7. Liu C and Wyman CE, The effect of flow rate of compressed hot water on xylan, lignin and total mass removal from corn stover. *Ind Eng Chem Res* **42**:5409–5416 (2003).
- Archambault-Leger V, Shao X and Lynd LR, Integrated analysis of hydrothermal flowthrough pre-treatment. *Biotechnol Biofuel* 5(49): (2012).
- Yang B, Gray MC, Liu C, Lloyd T, Stuhler SL, Converse AO *et al.*, Unconventional relationships for hemicellulose hydrolysis and subsequent cellulose digestion. ACS Sym Ser (Lignocellulose Biodegradation) 889:100–125 (2004).
- Wyman CE, Dale B, Elander RT, Holtzapple M, Ladisch MR and Lee YY, Coordinated development of leading biomass pre-treatment technologies. *Bioresource Technol* 96:1959– 1966 (2005).
- Yang B and Wyman CE, Pre-treatment: The key to unlocking low-cost cellulosic ethanol. *Biofuel Bioprod Bioref* 2:26–40 (2008).
- Mosier N, Wyman CE, Dale BE, Elander R, Lee YY, Holtzapple M *et al.*, Features of promising technologies for pre-treatment of lignocellulosic biomass. *Bioresource Technol* **96**:673–686 (2005).
- Gulati M, Westgate PJ, Brewer M, Hendrickson R and Ladish MR, Sorptive recovery of dilute acid ethanol from distillation column bottoms stream. *Appl Biochem Biotech* 57/58: (1996)

- Maiorella BL, Blanch HW and Wilke CR, Biotechnology report: Economic evalutaion of alternative ethanol fermentation processes. *Biotechnol Bioeng* XXVI:1003–1025 (1984).
- Haelssig JB, Tremblay AY and Thibault J, Technical and economic considerations for various recovery schemes in ethanol production by fermentation. *Ind Eng Chem Res* 47:6189–6191 (2008).
- Liu C and Wyman CE, Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery and enzymatic digestibility of cellulose. *Bioresource Technol* 96(18):1978–1985 (2005).
- Archambault-Léger V and Lynd LR, Fluid mechanics relevant to flow through pre-treatment of cellulosic biomass. *Bioresource Technol* 157:278–283 (2014).
- Shao X and Lynd LR, Kinetic modeling of xylan hydrolysis in co- and countercurrent liquid hot water flow-through pretreatments. *Bioresource Technol* **130**:117–124 (2013).
- Archambault-Léger V, Shao X and Lynd LR, Simulated Performance of Reactor Configurations for Hot-Water Pretreatment of Sugarcane Bagasse. *Chem Sus Chem* 7(9):2721–2727 (2014).
- 20. Humbird D, Davis R, Tao L, Kinchin C, Hsu D and Aden A, Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pre-treatment and Enzymatic Hydrolysis of Corn Stover. National Renewable Energy Laboratory, Golden, Colorado (2011).
- Aden A, Ruth M, Ibsen K, Jechura J, Neeves K, Sheehan J et al., Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. National Renewable Energy Laboratory, Golden, Colorado (2002).
- 22. Kazi FK, Fortman J, Anex R, Kothandaraman G, Hsu D, Aden A et al., Techno-Economic Analysis of Biochemical Scenarios for Production of Cellulosic Ethanol. National Renewable Energy Laboratory, Golden, Colorado (2010).
- Kumar D and Murthy GS, Impact of pre-treatment and downstream processing technologies on economics and energy in cellulosic ethanol production. *Biotechnol Biofuel* 4(27): 27–46 (2011).
- Dias MOS, Junqueira TL, Cavalett O, Cunha MP, Jesus CDF, Rossell CEV et al., Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. *Bioresource Technol* **103**(1):152–161 (2012).
- Rezende CA, Lima MAd, Maziero P, deAzevedo ER, Garcia W and Polikarpov I, Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnol Biofuel* 4(54): 1–19 (2011).
- Zafar S. Energy potential of bagasse. [Online]. BioEnergy Consult: Powering Energy Future (2013). Available at: http:// www.bioenergyconsult.com/tag/composition-of-bagasse/ [11 July 2014].
- 27. Lynd LR and Grethlein HE, IHOSR/Extractive distillation for ethanol separation. *Separ Technol* 59–62 (1984).
- 28. Rocha GJM, Goncalves AR, Oliveira BR, Olivares EG and Rossell CEV, Steam explosion pre-treatment reproduction and alkaline delignification reactions performed on a pilot scale

with sugarcane bagasse for bioethanol production. *Ind Crop Prod* **35**(1):274–279 (2012).

- 29. Laser M, Schulman D, Allen SG, Lichwa J, Antal MJ and Lynd LR, A comparison of liquid hot water and steam pre-treatments of sugar cane bagasse for bioconversion to ethanol. *Bioresource Technol* **81**:33–44 (2002).
- Kaar WE, Gutierrez CV and Kinoshita CM, Steam explosion of sugarcane bagasse as a pre-treatment for conversion to ethanol. *Biomass Bioenerg* 14(3):227–287 (1998).
- Young LY and Frazer AC, The fate of lignin and lignin-derived compounds in anaerobic environments. *Geomicrobiol J* 5:261–293 (1987).
- Carmona M, Zamarro MT, Blazquez B, Durante-Rodriguez G, Juarez JF, Valderrama JA *et al.*, Anaerobic catabolism of aromatic compounds: A genetic and genomic view. *Microbiol Mol Biol Rev* 73(1):71–133 (2009).
- Larsson S, Palmqvist E, Hahn-Hagerdal B, Tengborg C, Stenberg K, Zacchi G *et al.*, The generation of fermentation inhibitors during dilute acid hydrolysis of softwood. *Enzyme Microb Tech* 24(3/4):151–159 (1999).
- Klinke HB, Thomsen AB and Ahring BK, Inhibition of ethanolproducing yeast and bacteria by degradation products during pre-treatment of biomass. *Appl Microbiol Biot* 66:10–26 (2004).
- 35. Casey E, Sedlak M, Ho NWY and Mosier NS, Effect of acetic acid and pH on the cofermentation of glucose and xylose to ethanol by a genetically engineered streain of *Saccharomyces cerevisiae*. *FEMS Yeast Res* **10**(4):385–393 (2010).
- 36. Turn SQ, Keffer V and Staackmann M, *Analysis of Hawaii Biomass Energy Resources for Distributed Energy Applications*. University of Hawaii, Hawaii Natural Energy Institute, School of Ocean and Earth Sciences and Technology, Honolulu (2002).
- Programa das Nações Unidas para o Desenvolvimento (PNUD), Biomass Power Generation: Sugar Cane Bagasse and Trash, 1st edn, ed by Hassuani SJ, Leal MRLV, Macedo IdC, Piracicaba, Brazil (2005).
- Olivério JL, Novas tecnologias para biocombustíveis, in 9° Encontro de negócios de energia, São Paulo,14 de outubro (2008).
- 39. Seabra JEA, Taoa L, Chuma HL and Macedob IC, A technoeconomic evaluation of the effects of centralized cellulosic ethanol and co-products refinery options with sugarcane mill clustering. *Biomass Bioenerg* 34(8):1065–1078 (2010).
- 40. Chemical Engineering, *Plant Cost Index*. McGraw-Hill Publishing Co., Albany, NY (2012).
- Gnansounou E and Dauriat A, Techno-economic analysis of lignocellulosic ethanol: A review. *Bioresource Technol* 101(13):4980–4991 (2010).
- Headley RL, Pulp cooking developments focus on fiber yield, lower chemical use, in *Pulp & Paper*. Canadian Pulp and Paper (1996).
- 43. KPMG International. [Online] (2014). Available at: http://www. kpmg.com/global/en/services/tax/tax-tools-and-resources/ pages/corporate-tax-rates-table.aspx [20 March 2014].
- 44. Jaguaribe EF, Lobo PC, Souza WLd, Rocha RM and Nascimento ET, Better sell bagasse than surplus electricity? *Thermal Eng* 6(1):65–73 (2007).