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Conceptual net energy output for biofuel production from lignocellulosic biomass through biorefining☆

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ABSTRACT

There is a lack of comprehensive information in the retrievable literature on pilot scale process and energy data using promising process technologies and commercially scalable and available capital equipment for lignocellulosic biomass biorefining. This study conducted a comprehensive review of the energy efficiency of selected sugar platform biorefinery process concepts for biofuel production from lignocelluloses. The process data from approximately a dozen studies that represent state-of-the-art in cellulosic biofuel production concepts, along with literature energy input data for agriculture operations, were analyzed to provide estimates of net energy production. It was found that proper allocation of energy input for fertilizer and pesticides to lignocellulosic biomass and major agriculture or forestry products, such as corn and lumber in corn farming and lumber plantations, respectively, were critical. The significant discrepancies in literature data suggest studies are needed to determine energy inputs for fuel in farming and farm machinery. Increasing solids loading in pretreatment to at least 25% is critical to reducing energy input in a biorefinery. Post thermo-chemical pretreatment size reduction approach should be adopted for energy efficient woody biomass processing. When appropriate pretreatment technologies are used, woody biomass can be processed as efficiently as herbaceous biomass and agricultural residues. Net energy output for cellulosic ethanol was estimated to range approximately from −500–2000 MJ/ton biomass (HHV base); indicating that the energy input/output ratio is approximately 1:1 for cellulosic ethanol. However, net energy can reach approximately 4000–7000 MJ/ton of biomass when energy from lignin is included.

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1. Introduction

The concept of producing lignocellulosic biofuel, bioproducts, and chemicals through a biorefinery using lignocelluloses has been around for 70 years or more [1,2]. The recent interest in this old concept arises from the promises of mitigating climate change by substituting some biomass energy for petroleum or other fossil-fuel energy; achieving national energy independence and sustainable economic development; and advances in biotechnology in the past 2–3 decades. Geopolitical and national security reasons have greatly contributed to the need for seeking alternative energy, especially using domestic renewable and sustainable sources.

Several studies have suggested that biofuel from lignocellulosic biomass can be sustainably produced using modern technology coupled with sound policies [3,4]. The United States (U.S.) alone could sustainably produce 1.3 billion tons of biomass annually at some point in the future, 30% of which could come from woody biomass [5]. The theoretical ethanol production from 1.3 billion tons of biomass is about 130 billion gallons [6], or about 60% (40% using ethanol yield of 70 gallons/ton biomass) of current gasoline energy used in the U.S. With this potential, aggressive research strategies have been developed in the U.S. through various venues in recent years. For example, a workshop sponsored by the U.S. Department of Energy (U.S. DOE) in December 2005, focused on biochemical conversion of biomass to liquid fuel and produced a joint research agenda [7]. A second workshop sponsored jointly by the U.S. National Science Foundation (NSF), the American Chemical Society, and the DOE in June 2007 [8], focused on thermo-

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chemical conversion of biomass to liquid fuel. A third workshop sponsored by the U.S. Department of Agriculture (USDA) Forest Service (USFS) in December 2007 focused on sustainable production of forest biomass and woody biomass conversion technologies [9]. Major research and development investments have also been put into place around the world. The U.S. DOE established three bioenergy research centers to focus on fundamental of lignocellulose bioconversion with direct investment of US$375 million over five years. The USDA National Institute of Food and Agriculture (NIFA) recently funded five regional bioenergy coordinated agriculture projects (CAPs) totaling US$136 million for 5 years. Two CAPs of US$80 million total were focused on forest biomass. The U.S. DOE also established a loan guarantee program for building biorefineries. The private sector has also invested in biofuel technologies. For instance, BP invests significantly in the Bioenergy Science Institute hosted by the University of California-Berkeley. In China, the Chinese Academy of Sciences (CAS) established the Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT) with initial investment of US $50 million. The QIBEBT is currently expanded to the second phase with more investments. The European Union recently announced US$45 million funding for biorefinery research (EUROBIOREF)in 14 member countries through its Seventh Framework Program.

Much research effort has been made in the last three decades with many technological breakthroughs. However, the realization of the biorefinery concept remains a challenge. Economic performance has been a primary barrier to commercial deployment. Several techno-economic studies have been carried out [10–14]. Biorefinery economics are dictated by feedstock and capital equipment costs, as well as the performance and product portfolio of process technologies and competitive market restraints on selling price. The demand for energy is in general inelastic. Most forms of energy are bulk commodities that compete for market share on the basis of their cost and utility. This suggests that cost, utility and profitability of bioenergy will be the primary forces driving or limiting the implementation of biorefinery technologies. Unfortunately, biofuel has to compete with petroleum-based liquid transportation fuel currently at a relatively low market price though large fluctuations in terms of crude oil price were observed over the last 5 years. Oil price will be expected to grow in the long term. As a result, a major obstacle is still economics [15], and cost competition will continue to prevail so long as energy markets are primarily bulk commodity markets. However, the price of petroleum is dictated by many factors other than the actual production and delivery costs, such as investor speculation, geopolitics, and government tax policies and subsidies in different forms [16,17]. Therefore, sound government energy policies and a funding strategy are vital to the successful development of a vibrant bio-based economy in addition to advancing biorefinery technologies.

Energy efficiency can be a long term driving force in developing bioenergy technologies despite economics being the short term driving force [15]. This review is therefore focused on the efficient liquid bioenergy production from lignocellulosic biomass through biochemical conversion, one of the major pathways for lignocellulosic biomass conversion to energy. Lignocellulosic biomass has a typical carbohydrates content of approximately 65%. The biochemical conversion or the sugar platform relies on hydrolyzing carbohydrates to sugars to produce energy and various chemicals as schematically shown in Fig. 1. A significant amount of the available literature has been focused on sugar/biofuel production from lignocellulosic biomass that covers pretreatment [18–33], hydrolysis and saccharification [34–45], fermentation [46–53], metabolic engineering [54–59], plant science [60–64], and catalysis [65–70]. The issue of bioenergy production has also been studied using life cycle analysis [71–78]. However, these studies rely on estimated energy inputs, rather experimental data, for biorefinery operation that shares approximately more than 80% of the total energy input. The reported final net energy output varied significantly. Most studies do not report net energy output and process energy balance data [79,80]. Unfortunately, if a biorefinery is going to be an energy operation to substitute petroleum energy production, without net energy output from carbohydrates it is worse off than a very energy intensive traditional pulp mill, where carbohydrates are converted to fiber and lignin is used to produce power for mill operation through combustion.

Commercial conversion process scalability is vital. Despite several lignocellulosic ethanol demonstration plants being built or currently under construction with the sponsorship of U.S. DOE, few

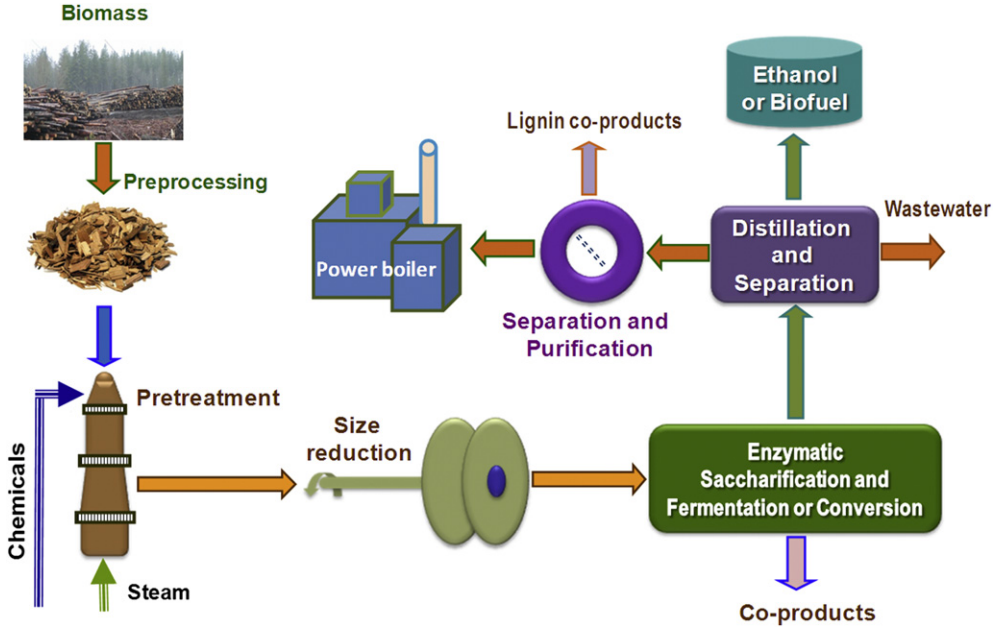

Fig. 1. A schematic diagram shows typical biorefinery process steps.

comprehensive published studies have been carried out on pilot scale using promising process technologies and commercially scalable and available capital equipment. Most of the reported studies on promising process technologies are at laboratory scale [28,31,50,79,81–87]. The authors are not aware of any published experimental study that span the entire production process from upstream feedstock harvest to downstream product separation even at laboratory scales. In view of these facts, we present this comprehensive review that uses available energy input data from a dozen of laboratory biorefinery studies to provide objective information on energy efficiency of biorefinery process concepts for fuel ethanol production from lignocellulosic biomass.

We will walk the readers through the entire biofuel production process using the sugar platform that relies on the conversion of carbohydrates in lignocelluloses to sugars by hydrolysis in the pretreatment and subsequent enzymatic saccharification step. Specifically,

(1) We will present feedstock heating values and carbohydrate contents to provide the amounts of energy and sugars available among different lignocellulosic feedstock.
(2) We will point out the key energy barriers of a biorefining in order to focus on process energy efficiency. We will discusses energy consumption for lignocellulosic biomass size reduction, the prerequisite step for any biomass conversion technology, energy for biomass thermo-chemical pretreatment and mixing for high solids enzymatic saccharification.
(3) We will define the concept of energy efficiency for pretreatment and for biofuel production. We will point out the key steps needed to be taken to improve energy efficiency. Data on energy inputs for agriculture operations available in the literature will be integrated into our analyses.

2. Energy stored in lignocellulosic biomass

2.1. Biomass composition and heating value

Lignocellulosic biomass stores solar energy through photosynthesis, the process that can sequester carbon dioxide, a green house gas. Typically photosynthesis converts less than 1% of the available sunlight to chemical energy stored in the bonds of structural biomass components [88]. When this energy is released through thermo-chemical reactions such as combustion or gasification, it produces carbon dioxide and water. The process is cyclical as the carbon dioxide is then available to produce new biomass. The fundamental sustainability of biofuel from biomass is based on the cyclical or renewable nature of biomass. However, it must be pointed out that there is a time lag between the instant release of carbon dioxide from using bioenergy and photosynthesis, which draws debates on the renewability of lignocellulosic biomass.

The plant biological properties dictate plant pathway and efficiencies of photosynthesis [88], i.e., plant growth rate as well as the chemical compositions of a plant. As a result, the energy content and energy density varies with plant biomass and are dictated by plant and cell wall structure. In general woody biomass including both softwood and hardwood species has a higher lignin and cellulose content and density than herbaceous biomass and agricultural residues such as switchgrass, corn stover, and straw. The high lignin and cellulose contents in woody biomass produced tightly bound cellulosic fibers to sustain its large structure compared with herbaceous biomass fibers [88]. Woody biomass also typically has lower ash content than herbaceous biomass and agricultural residues. Softwood species have higher lignin content than hardwood species. Typical chemical compositions of lignocellulosic biomass are listed in Table 1. The relatively high

Table 1
List of chemical compositions and heating values of different types of lignocellulosic biomass. Hol = Holocellulose; L = Lignin.

	Composition (%)								HHV × 10^{-3} (MJ/ton)				
	Ash	Extractives	Lignin	Glucan	Xylan	Mannan	Holocellulose	Hol/L	Measured	[Eq. (3)+(4)]/2	Eq. (7)	Eq. (11)	Eq. (12)
Spruce[a]	0.3		28.3	43.2	5.7	11.5	64.5	2.279			18.8		
Lodgepole pine[a]			29.1	39.8	6.8	10.1	61.9	2.127			18.5		
Ponderosa pine[a]			26.9	41.7	6.3	10.8	64.5	2.398	21.2		18.4		
Douglas-fir[b]	0.4		32.0	44	2.8	11	65.2	2.038	17.4		19.9		
Loblolly pine[b]	0.4		28.0	45	6.8	11	66.8	2.386	20.0		19.1		
Red pine[b]	0.4		29.0	42	9.3	7.4	62.9	2.169			18.7		
Red maple[b]	0.2		24.0	46	19.0	2.4	68.5	2.854			18.3		
Aspen[a]			20.2	45.6	16.4	1.4	63.4	3.139			16.4		
Salix[c]	0.9		26.4	41.4	15.0	3.2	63.1	2.390			18.0		
Yellow poplar[d]	1.9	2.8	23.3	42.1	15.1	2.4	61.1	2.622			17.7		
Eastern cotton wood[d]	1.0	2.4	25.6	42.2	13.4	2.0	58.8	2.297	19.6	19.5	17.8	19.9	19.7
Hybrid poplar DN34[d]	0.8	2.1	23.9	43.7	17.4	2.9	65.2	2.219	19.5	19.4	18.6	19.5	19.7
Eucalyptus saligna[d]	1.2	4.2	26.9	48.1	10.4	1.3	60.8	2.258	19.5	19.3	19.1	19.8	19.7
Hybrid poplar DN5[a]			22.9	39.1	17.3	3.9	61.4	2.680			16.8		
Hybrid poplar NE222[a]			23.5	40.8	16.4	3.8	61.9	2.635			17.0		
Hybrid poplar NM6[a]			25.2	39.4	15.8	3.7	60.0	2.382			17.1		
37-sugarcane bagases[d]	3.7	3.8	23.1	39.0	22.1	0.4	63.9	2.769	19.4	18.8	18.5	19.6	19.2
38-sugarcane bagases[d]	2.8	1.5	24.1	43.4	23.1	0.3	68.9	2.858	19.0	18.8	18.9	19.4	19.3
39-sugarcane bagases[d]	4.0	2.0	24.1	42.6	23.1	0.3	68.0	2.829	19.0	19.0	18.9	19.5	19.2
151-sugarcane bagases[d]	4.0	4.4	23.1	38.6	20.4	0.3	61.6	2.667	18.4	18.3	18.3	18.9	18.8
46-Corn stover[d]	11.0	11.9	18.2	30.6	16	0.5	49.7	2.734	18.2	18.9	17.3	18.2	18.2
47-Corn stover[d]	11.5	4.8	20.2	38.1	20.3	0.4	61.5	3.376	18.4	18.8	16.5	18.4	18.5
48-Corn stover[d]	11.4	3.3	19.3	36.5	19.0	0.5	59.3	3.082	18.4	18.2	16.5	18.0	17.7
50-Corn stover[d]	12.5	3.9	18.2	37.1	20.3	0.5	61.3	3.377	17.9	18.8	16.7	19.1	18.5
74-Switchgrass[d]	5.8	17.0	17.6	31.0	20.4	0.3	55.4	3.152	18.6	19.1	19.8	18.4	18.6
86-Switchgrass[d]	6.2	7.9	20.5	33.0	21.6	0.4	58.8	2.870	19.0	18.8	18.2	19.2	19.0
94-Switchgrass[d]	5.7	13.5	17.4	34.3	22.4	0.3	60.5	3.489	18.6	19.0	19.5	18.6	18.5
152-Wheatstraw[d]	10.2	13.0	16.9	32.6	19.2	0.3	55.3	3.280	17.4	18.4	18.3	17.3	17.4

[a] From our own work: spruce [20], lodgepole pine [160], aspen [83], hybrid poplar [161].
[b] From Pettersen [162].
[c] From Sassner [123].
[d] From US DOE Biomass program database http://www1.eere.energy.gov/biomass/feedstock_databases.html.

holocellulose content of woody biomass is favorable for biochemical conversion to biofuel through the sugar platform.

Lignin is a key source of biomass energy though lignin content is approximately 30–40% of holocellulose content in lignocelluloses (Table 1). The heating value of lignin is about 50% higher than that of holocellulose [89], i.e., heating values for lignin and holocellulose are 26.7 and 17.5 $\times$ 10^3 MJ/ton, respectively. The heating value of wood extractives was reported to be 32.3 $\times$ 10^3 MJ/ton [90]. Several approaches have been taken to predict heating values of biomass [91]. The proximate analysis uses fixed carbon (FC) and volatile matter (VM) to estimate heating value [91–94]. The chemical composition approach uses the content of lignin, holocellulose, extractives, and ash to determine biomass heating value [89,92,94–96]. A simplified version of this approach only uses lignin content to develop linear correlation with the consideration of extractives [95,97]. The elemental approach relates heating value to the composition of chemical elements of biomass [89,91,92,98,99]. It may be the most accurate approach simply because more information is provided. A chemometric analysis was applied to a biomass heating value database of 154 data set [100] which resulted in a correlation to accurately predict biomass heating values. The correlation only requires the information of carbon (C), hydrogen (H) and nitrogen (N) [101]. Table 2 lists typical correlations for the prediction of biomass heating values using these three approaches. Except for the correlation from chemometic analysis [101], (Eq. (12)), the listed correlations were chosen because they all have physical meaning, i.e., the coefficients represent the actual contribution of an element or component to biomass heating value. This can be clearly seen from Eq. (7) in which the coefficients for lignin, holocellulose, and extractives are the heating values of these components, respectively. The coefficients for the same element or component in different equations in the same form are similar. As a result, the accuracies of these correlations are more or less the same when compared with the measured data.

The heating values listed in Table 1 were calculated using some of the correlations listed in Table 2. The available measured data were also listed. The database from the US DOE Biomass Office (http://www1.eere.energy.gov/biomass/feedstock_databases.html) has all the information needed for the calculation of heating values using all the equations listed in Table 2. Furthermore, the measured heating values are from the same DOE database of composition. The results indicate that softwoods have high heating values because of high lignin contents. Similarly, the heating values of woody biomass are higher than herbaceous and agricultural biomass due to higher lignin content. The results in Table 1 also suggest that approximately 11 $\times$ 10^3 MJ/ton of biomass energy is from holocellulose (carbohydrates) and 6 $\times$ 10^3 MJ/ton is from lignin. An efficient lignocellulose bioconversion process through the sugar platform for energy production needs to produce net energy from lignin as well as from carbohydrates.

Table 2
List of equations for the calculation of heating value of lignocellulosic biomass using different approaches. FC = fixed carbon, VM = volatile matter, E = extractives, Hol = Holocellulose, L = Lignin, C = carbon, H = hydrogen, O = oxygen, S = sulfur, N = nitrogen, all in percent.

Equation	Correlation of HHV $\times$ 10^{-3} (MJ/ton)	Source
Proximate analysis		
(1)	HHV = 19.91−0.232Ash	[91]
(2)	HHV = 0.196FC + 14.12	[92]
(3)	HHV = 0.312FC + 0.153VM	[92]
(4)	HHV = 0.354FC + 0.171VM	[93]
Chemical composition analysis		
(5)	HHV = 0.089L + 16.82	[97]
(6)	HHV = 0.085L + 17.44 for extractive free wood	[95]
(7)	HHV = 0.174Hol + 0.266L + 0.322E	[96]
(8)	HHV = 0.174Hol + 0.266(100 − Hol) for extractive free wood	[89]
Elemental analysis		
(9)	HHV = 0.326C + 3.46	[91]
(10)	HHV = 0.335C + 1.423H−0.154O − 0.145N	[92]
(11)	HHV = 0.349C + 1.178H + 0.100S−0.103O − 0.015N−0.021Ash	[99]
(12)	HHV = $0.00355C^2$ − 0.232C − 2.23H + 0.0512C $\times$ H + 0.131N + 20.6	[101]

2.2. Volumetric energy density of biomass

Biomass is a low density materials, therefore, transportation energy costs are generally dictated by volume rather weight depending on the means of transportation and local regulation [102]. Consequently, volumetric energy density of biomass can be important because it directly relates to energy consumption and cost for biomass transportation. Packing density is more relevant to biomass transport than the density of biomass itself. In the U.S., the maximal bulk density based on the maximal legal allowable loading weight for trucking is 143 kg/m^3 [102]. Typical packing densities for nonwoody biomass are within 100 kg/m^3 [103], therefore, transportation of nonwoody biomass is limited by volume. The packing density of woody biomass, such as wood chips, is around 350 kg/m^3 depending on moisture content [102]. Therefore, the packing density of woody biomass is approximately three times that of herbaceous and agricultural residues and is not the limiting factor for transportation.

3. Analysis of net energy production through biorefinery

3.1. The analytical approach

Published energy data on agriculture operations were used in this study. Energy inputs for key biorefinery process operations were also based on published literature. Our approach examines the entire energy production process including agriculture, transportation, and processing to evaluate net energy production. The energy in biomass as the primary energy source is not used as an input. Environmental aspects will be not discussed in this review as we are focused on energy production. At first pass, we will not differentiate renewable or nonrenewable energy as some studies did in order to emphasize the displacement of nonrenewable energy by renewable energy [73,76,78]. Because we try to examine the quantities of energy first before evaluating the qualities, values, and utilities of energy whether it comes from renewable or nonrenewable. The quantity of energy is important because the production of renewable energy is not sustainable without net energy output. We might as well use the nonrenewable energy directly without investing the production of renewable energy. In our first pass analysis, we assume only energy is produced without considering co-product production. Credits for co-products from literature are then added to our first pass analysis. This approach is taken because: (1) such analysis provides a clear understanding of the role of co-products in the overall energy balance of biomass biorefinery (i.e. the co-product allocation can have a significant impact on net energy production [104]); and (2) estimating the energy efficiency of co-product production is difficult because there is no commercial biorefinery operation that can provide a foundation for such an effort.

3.2. Energy inputs for agriculture operations

3.2.1. Analysis of literature data on agriculture energy input

The energy inputs for agriculture operations were mainly based on the EBAMM model published in Science by Farrell et al. [78].

However the basic data, such as energies for producing unit kg of nitrogen based fertilizer or herbicide, were updated using the U.S. DOE Argonne National Laboratory GREET 1-2011 database. Two additional recent works were also included. The first work by Schmer et al. reported energy input data from actual switchgrass agriculture experiments on ten farms [77]. The data for post-planting were the average of the 10 farms studied. The second work was a European study recently published [71]. Corrections were made to errors in the study based on the fundamental data provided in [71]. The GREET database was not applied to these two studies.

The following points can be made about energy inputs for biomass agriculture operations from the results of the 11 studies listed in Table 3. First, fertilizer, especially nitrogen based fertilizer, consumes a significant amount of energy. Most studies reported approximately 7500 kJ/ha for nitrogen in agriculture operation. The data by Schmer et al. [77] based on operations at 10 switchgrass farms and the estimate by Farrell et al. [78] for switchgrass are much lower. It appears that the high energy input for nitrogen is probably based on the nitrogen application for growing corn. This is corroborated by the very low energy input for nitrogen of 2900 kJ/ha obtained from 10 switchgrass farms [77]. When producing biofuel/ethanol from corn stover, the energy for fertilizer needs to be properly allocated to both corn and stover. It is not justified to allocate 100% of the energy input for fertilizers and pesticides to corn stover. Another approach to address this issue is to use corn as a major agriculture co-product and provide proper energy credit to cellulosic ethanol production as exercised by Lou et al. [71].

The second largest energy input for agriculture operation is diesel, natural gas, gasoline, LPG, and electricity that is reported in the range of 3700–8500 kJ/ha for most studies. The average actual data from 10 switchgrass farms by Schmer et al. [77] were significantly lower at less than 1000 kJ/ha. It appears again that the high energy input is based on growing corn, which did not separate the energy input for corn from stover similar to the case for fertilizers and pesticides as discussed above.

Third, there are significant discrepancies in the energy inputs for farm machinery. The work by Patzek [105] and Pimentel and Patzek [72] reported more than an order of magnitude higher energy inputs of 6100 and 4300 kJ/ha, respectively, than most of the other studies. The European study of Lou et al. [71] reported energy input for farm machinery of 1100 kJ/ha that included machinery for corn co-product production. The low energy inputs for farm machinery in the EBAMM model for most studies [78,106–108] were from the same source [107]. The data from 10 switchgrass farm operations by Schmer et al. also reported low energy inputs [77]. Because the discrepancies within the literature are very significant and limited data are available, this energy input needs to be further studied experimentally to obtain a more accurate estimate.

Significant variations in energy input for seed among the studies were also observed. Some studies did not report energy input for seed. The three studies [72,105,108] with high energy input for seed were either from the same source or using similar estimation methods. The average data of Schmer et al. [77] and the data from the European study of Luo et al. [71] both supported a low energy input for seed.

3.2.2. Analysis scenarios for agriculture energy input

The observations presented in the previous subsection suggest that more experimental data from agricultural operations are needed to accurately account for agriculture energy input. These observations also suggest that different approaches should be taken to account for agriculture energy input in biofuel/ethanol production using corn stover versus using switchgrass. This is because corn itself is a major product while no major co-products are produced in farming of energy crops such as switchgrass. Similarly, accounting of agriculture energy input for forest thinnings or lumber harvest residues should be different from that for dedicated woody energy crops. This is because the forest thinnings or harvest residues are only a by-product of commercial plantations that produce major products for paper, lumber and construction materials. The total energy inputs for growing corn and commercial plantations should be properly allocated to their respective major products.

We will take two approaches in this study to address the issue discussed above. First, the energy inputs for corn stover and forest thinnings or harvest residues are only the energy used directly for biomass acquisition, such as harvesting, transporting, storage, etc. Energy inputs for fertilizer, pesticide, seeds, road construction, are all allocated to corn or lumber productions. This approach assumes that the harvested corn stover and forest thinnings are wastes that need to be disposed in corn farming and commercial tree plantations, respectively. However, re-fertilization is applied to replace 50% of the nutrient losses due to collection of forest residues based

Table 3
Energy input in MJ/ha for biomass agriculture operations (except for the work by Schmer [77] and Luo [71]) data are from Transportation Sustainability Research Center, University of California at Berkeley.

	Patzek [105]	Pimentel and Patzek [72]	Shapouri and McAloon [106]	Graboski [107]	Dias de Oliveira et al. [108]	Wang [111]	Farrell et al. [78]	Farrell et al. [78]	Schmer et al. pPost-planting [77]	Schmer et al. eEstablished [77]	Luo et al. [71]
	Corn	Corn	Corn	Corn	Corn	Corn	Corn	Switchgrass	Switchgrass	Switchgrass	Corn + Stover
YEAR published	**2004**	**2005**	**2004**	**2002**	**2005**	**2001**	**2006**	**2006**	**2008**	**2008**	**2009**
Nitrogen	7380	7589	7423	7469	7242	7277	7423	2480	2900	0	7988
Phosphorus	886	922	903	783	908	727	903	30		0	
Potassium	829	683	877	571	781	542	877	30		0	
Lime	583	1318	0	369	445		56	0		0	1067
Herbicide	673	1643	734	641	795	737	734	110	474	598	167
Insecticide	341	885	66	47	316	66	66	0			
Seed	1968	2176	228	215	2048		228	0	99	406	158
Transportation	400	707	73	738	0	168	504	36	42		398
Gasoline, diesel, natural gas, LPG	5947	5891	5432	6450	5883	8510	5432	3737	882	555	5481
Electricity	688	143	820	1571	657	225	820	618		214	382
Irrigation		1339	49				49	0			
Farm machinery	6050	4259	320	320	320	320	320	320	283		1074
Packaging	74	74	74	74	74	74	74	74	17		
Total energy input	**25819**	**27627**	**16999**	**19249**	**19466**	**18646**	**17486**	**7434**	**4697**	**1770**	**16715**

on the estimates of Eisenbies et al. [109]. Second, using the approach by Luo et al. [71] that provides energy credit to a major product (i.e. corn), when using the total energy input for agricultural operation in growing corn. Using these approaches, we created 3 possible scenarios of determining energy input for agriculture operation for cellulosic biofuel/ethanol production using corn stover, switchgrass, and woody biomass.

Scenario (I): corn stover and forest thinning or residues are simply waste. The energy input is the energy to collect and transport. The energy input of 2094 MJ/ha for harvesting and transport of corn stover is based on the data of Lou et al. [71]. The energy input of 4936 MJ/ton for forest residues is based on brash bale harvesting (740 MJ/ton for harvesting and chipping +53 MJ/ton for transporting) reported by Whittaker et al. [110] using 14 year rotation. We excluded the road construction and maintenance energy (355 MJ/ton) as this input should be allocated to lumber and pulp wood because we treat residues as purely waste in this scenario. We added 179 MJ/ha to replace 50% of the nutrients due to removal of forest residues [109].

Scenario (II): corn stover has a major agriculture product – corn. Therefore agriculture energy input for corn stover should be the energy input for growing corn. The average energy input 18094 MJ/ton for the 6 corn farming studies [71,78,106–108,111] listed in Table 3 is used with an energy credit for corn of 85.2 MJ/L ethanol [71].

Scenario (III): energy crops with no major product, such as switchgrass and woody energy crop. The energy input for switchgrass of 4697 MJ/ha is the average energy measured at 10 switchgrass farms for the post-plating years [77]. Keoleian and Volk reported average energy input for woody energy crops of 355 MJ/ton [112]. This number is significantly lower than the 1177 MJ/ton for collecting whole trees in forest thinning operations reported by Whittaker et al. [110] using LCA analysis. The average of these two studies of 766 MJ/ton (7660 MJ/ha) was used.

3.3. Bioconversion process technologies

Biorefining in a production concept using lignocelluloses as feedstock, as opposed to petroleum, to produce liquid transportation fuel and a variety of chemicals is analogous to petrochemical refining, although the processes are quite different. Biochemical conversion of lignocellulosic biomass, generally known as the sugar platform, relies on the conversion of carbohydrates to sugars by hydrolysis during the pretreatment and the subsequent enzymatic saccharification step. The pretreated lignocelluloses have a relatively open structure that is accessible to cellulase enzymes mainly through pores in lignocellulosic fibers [45]. The cellulose binding module (CBM) of a cellulase binds cellulase to fibers while the catalytic domain of the cellulase is responsible for hydrolyzing cellulose (made of a chain of glucan unit) into glucose to achieve saccharification [113], which will be discussed in Section 3.3.2. The resulting sugars can be converted to alcohol or other liquid hydrocarbons along with chemicals through fermentation, catalysis, or other chemical means. Lignin can be converted to power or energy through combustion or gasification and to other co-products by further processing. A schematic diagram of this bioconversion process is shown in Fig. 1. The pretreatment step is required to remove the physical and chemical structural barriers of lignocellulosic biomass to cellulase enzymes to facilitate carbohydrate saccharification, the key to the sugar platform. Mother nature produces lignocellulosic biomass as structural materials with strong natural resistance, the so called recalcitrance [114,115], to mechanical, enzymatic and microbial deconstruction. A pretreatment step is often applied through mechanical and thermo-chemical means to remove this recalcitrance. Pretreatment and enzymatic saccharification along with downstream distillation and separation are the most energy intensive steps. Therefore it is worthwhile to present technological aspects of these processes to obtain better understanding of energy input for the entire biorefinery operations. Our analysis will be based on ethanol fermentation because of the availability of data in the published literature and the maturity of yeast fermentation technologies.

3.3.1. Pretreatment of lignocellulosic biomass

Biomass pretreatment includes both physical [24] and thermochemical processes [18,19,25,115]. Physical pretreatment refers to the prerequisite biomass size reduction step. An ideal thermochemical pretreatment process should be mild with low energy input. Yet it is capable of (1) effectively fractionating different lignocellulosic components, i.e., cellulose, hemicelluloses, and lignin, (2) producing a solid substrate with excellent enzymatic digestibility and a hemicellulosic liquid stream containing low degradation and inhibitive products to downstream conversion through fermentation or catalysis, and (3) a lignin fraction with potential for value added co-products. As a front end process, pretreatment dictates downstream processing and the utilization of different lignocellulosic fractions for co-product development. Below are a few of the most studied and promising thermochemical pretreatment processes.

Dilute acid pretreatment: It was developed based on the "Madison process" of acid hydrolysis of wood at the USFS, Forest Products Laboratory, in the 1940s [1,2]. It is the most widely studied pretreatment method. Hot water pretreatment is a special case of dilute acid pretreatment [19]. Major efforts in developing the dilute acid process were carried out by the National Renewable Energy Laboratory (NREL) in the U.S. [10]. Typical reaction conditions were temperatures of 160–190 °C. The NREL operation uses a high solids loading of size reduced corn stover with approximately an L/S = 2.3 for a short period of 1–10 min pretreatment. It is then followed by a flashing step, similar to steam explosion (see description below). For woody biomass applications, significant wood size reduction is prohibitive due to expensive energy costs [115,116], as will be discussed later in the text; wood chips rather than fiberized material is the preferred size range based on energy efficiency. For example, at the USFS Forest Products Laboratory, we used L/S of 3 to pretreat commercial sized aspen wood chips at 170 °C with sulfuric acid charge of 1.1% for 20–30 min [83,117]. We achieved excellent sugar recovery and ethanol yield with a moderate enzyme loading of 10 FPU/g glucan and a conventional *Saccharomyces cerevisiae*.

Dilute acid pretreatment is not effective for softwoods using conventional single stage short duration reactions. Enzymatic cellulose conversion efficiency was only approximately 40% when softwood (spruce and lodgepole pine) wood chips were pretreated at 180 °C with L/S = 3–4 followed by disk milling [20,116]. Sugar recovery can be increased at the expense of increased energy consumption, for example, by using a two-stage pretreatment (with fresh sulfuric acid solution in each stage) at 190 and 210 °C [118]. This is not much different from continuous circulation of fresh acid solution in acid hydrolysis of wood practiced in the 1940s using the "Madison Process" that also achieved excellent sugar recovery [1,2].

Catalyzed steam explosion: Early excellent work on process optimization and process fundamentals of SO_2-catalyzed steam explosion was conducted by Forest Research Institute of New Zealand [119,120]. Research and development on acid-catalyzed steam explosion were continued at two research groups: Lund University of Sweden [121–124] and University of British Columbia of Canada [30,125]. A comprehensive review on catalyzed steam explosion for woody biomass pretreatment was presented in one of our previous work [19]. The process uses a catalyst, such as sulfuric

acid and/or sulfur dioxide, with steam followed by a thermal flashing process (rapid depressurization) to achieve chemical pretreatment and physical-size reduction in one step. Although acid-catalyzed steam pretreatment can produce satisfactory enzymatic saccharification efficiency when applied to hardwoods, its effectiveness on softwoods is less satisfactory without applying the two-step explosion process [28,118,122,124]. Steam explosion pretreatment is energy intensive, especially when applied to softwood species at elevated temperatures of above 200 °C. Its commercial scalability yet needs to be demonstrated.

Sulfite pretreatment to overcome recalcitrance of lignocelluloses (SPORL): The SPORL process was recently developed at the USFS Forest Products Laboratory and the University of Wisconsin-Madison [20,21,50,81,83]. The published works in laboratory studies were practiced in aqueous batch reactions using sulfite or bisulfite (1–9% on wood) and sulfuric acid to adjust pH. However, bubbling sulfur dioxide into alkaline solution is best suited for commercial applications as practiced in the pulp and paper industry for sulfite pulping [126]. Pretreatment can be carried out in a temperature range of 160–190 °C for a period of 10–60 min or longer. Pretreatment L/S as low as 1.5 (solids loading of 40%) can be carried out though most of the reported studies used L/S = 3 (solids loading of 25%). Enzymatic saccharification efficiency over 90% can be achieved even when applied to softwoods [20,116]. Ethanol yields over 270 L/ton and preliminary mass and energy balance (Fig. 2) were reported [50,81]. Furthermore, lignin sulfonation has the potential for developing value added co-products.

The advantages of SPORL over conventional dilute acid pretreatment for energy production efficiency were demonstrated [83,117,127] especially at high solid processing [83]. Furthermore, SPORL process generates lower amounts of fermentation inhibitors, such as furfural and HMF [21,83,117,127] than dilute acid pretreatment. When compared with acid-catalyzed steam explosion and organosolv pretreatment, the pretreatment energy efficiency of SPORL is about 30 and 15% greater, respectively [19]. SPORL is developed based on sulfite pulping with proven commercial scalability and known technological and environmental risks.

Solvent based pretreatments: Organosolv [31,128], ionic liquid [129–131], and acid solvent [132], are a few examples using solvent to dissolve lignocelluloses in order to fractionate different components of biomass for bioconversion. The ethanol organosolv process is probably most studied among all solvent based pretreatment methods. Both sulfuric acid [31] and sulfur dioxide [128] were used with ethanol. Major development of the sulfuric acid-ethanol process for biorefining applications was carried at the University of British Columbia, Canada. In the sulfuric acid-ethanol process, typical reaction temperature varied from 170 to 190 °C for 60 min using L/S ranges 4 to 7. For the sulfur dioxide-ethanol process, the typical reaction temperature is 135 °C with L/S of 6. The resultant cellulosic substrates have excellent enzymatic digestibility. The lignin has excellent purity. The lignin from SO_2-ethanol pretreatment is sulfonated. The main drawback of these two organic solvent processes is the recovery of ethanol which requires a significant amount of energy input. In general, solvent based processes including ionic liquid pretreatment require a relatively large L/S to dissolve biomass and are expensive for solvent recovery.

Alkaline based pretreatments: Alkaline pretreatments do not produce common fermentation inhibitors, such as furfural and HMF, in pretreatment hydrolysates, which is beneficial for downstream fermentation. The ammonia based pretreatments, ammonia-fiber expansion (AFEX) [33] and aqueous ammonia or ammonia-recycle percolation (ARP) [32], produced good sugar and ethanol yield after enzymatic saccharification from corn stover [26]. However, both processes are not very effective when applied to woody biomass [32,80,133]. The high dosage of ammonia application (on the order of 100 wt% biomass) in AFEX pretreatment requires effective ammonia recovery technology. Technologies for commercial scale production using the AFEX process needs to be developed. The main drawback of lime pretreatment [134] is equipment-scaling in commercial applications. Sodium hydroxide based alkaline method [22] requires an expensive chemical recovery operation in addition to the unremarkable performance in enzymatic saccharification efficiency, especially applied to softwood species.

3.3.2. Enzymatic saccharification and fermentation

Enzymatic saccharification of cellulose in the pretreated lignocellulosic solid substrate is a step improvement to acid hydrolysis [1,2]. Most published studies used commercial cellulase cocktails derived from *Trichoderma reesei* that mainly consisted of three types of cellulases; endoglucanases, exoglucanases that include both cellobiohydrolase I and cellobiohydrolase II, and β-glucosidases. Endoglucanases randomly cleave β-1-4-glucosidic bonds to shorten cellulose chain length and produce reducing cellulose ends. Cellobiohydrolases produce cellobiose by attacking cellulose from

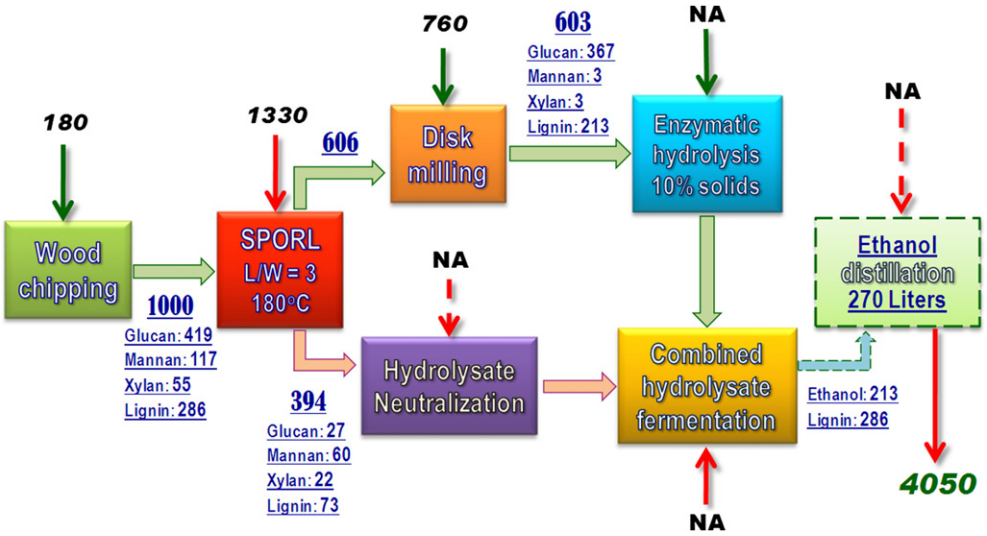

Fig. 2. A block diagram [50] showing process mass and energy balances for ethanol production from lodgepole pine by SPORL pretreatment. Unless indicated, energy data (bold italic font with vertical arrows) are in MJ/ton wood and mass data (underlined) are in kg. "NA" stands for experiments were not conducted and data were not available.

the reducing chain ends (cellobiohydrolase I) as well as from the nonreducing ends (cellobiohydrolase II). β-glucosidases convert cellobiose into glucose [34,113,135]. Studies have been conducted to optimize cellulase formulation based on a specific substrate [136,137]. Thermophilic enzymes have also been developed to increase the rate of lignocellulose liquefaction to accelerate enzymatic saccharification especially under high lignocellulose solids loadings [138].

Enzymatic saccharification and fermentation needs to be conducted at high solids loadings to produce high titer of sugar and therefore biofuel/ethanol titer to reduce energy cost for downstream distillation and separation. Mechanical mixing of high solids materials is required for effective liquefaction and enzymatic saccharification. Despite numerous studies reported on enzymatic saccharification and fermentation of lignocelluloses, few studies were conducted at high solids loadings of >15% with resultant ethanol titer of >40 g/L. The reported studies on high solids saccharification and fermentation were conducted at laboratory scale with low conversion efficiencies unless very high cellulase loadings were applied [139–142]. Furthermore, cellulose conversion efficiency decreased rapidly as substrate solids loading was increased [139]. Recently, a highly digestible SPORL substrate of aspen was saccharified at 18% solids with cellulase loading of only 10 FPU/g glucan using a torque rheometer [83]. Excellent ethanol yield (76%) and titer (59 g/L) was obtained using a conventional *S. cerevisiae*. The understanding of the effect of substrate digestibility on cellulose conversion efficiency under high solids loadings is very limited [83]. The practice of quasi-simultaneous enzymatic saccharification and fermentation (q-SSF) can significantly reduce product (sugar) inhibition [143], and has been widely adopted [83,139].

Mixing mechanism is a major part in scaling up enzymatic saccharification and fermentation technologies. Different mixers have been investigated [83,139,140,144,145]. Despite industrial applications of different mixers having been in practice, the scalability of these mixers for mixing lignocelluloses needs yet to be proven and their energy efficiencies also need to be verified. The torque rheometer provides similar mixing action as a commercial twin screw extruder, but the short residence time in the twin screw extruder requires a second mixing stage. From the reported time-dependent energy and torque data [83,139], it appears that high shear mixing is only required for a short period of time to liquefy solid lignocelluloses. Therefore, a combination of high shear mixing, such as that created by a twin screw extruder, and a low energy intensive mixing, such as that in a tumbling bed, may be what is needed for commercial scale high solids enzymatic saccharification and fermentation. Research at both laboratory and pilot scales needs to be carried out to demonstrate this concept.

3.3.3. Downstream separation and processing

Distillation followed by dehydration is still the primary approach for separation of alcohol based biofuels such as ethanol. Recent advances included membrane technologies as described by Vane [146–148]. The deployment of highly energy efficient membrane based technologies for biofuel downstream separation is critical to overall energy efficiency as will be discussed later in the text.

3.4. Energy inputs for biorefinery operations

3.4.1. Energy input and efficiency for pretreatment of lignocellulosic biomass

Physical pretreatment – size reduction – of herbaceous biomass can be easily achieved through hammer milling with typical energy costs within 50 kWh/ton (180 MJ/ton) [149,150]. However, size reduction of woody biomass is much more energy intensive. Typical energy consumptions of milling wood chips into fibers are approximately 500–800 kWh/ton (1800–2880 MJ/ton) [116,150,151]. These energy levels are equivalent to 25–40% of the thermal energy stored in the ethanol produced assuming ethanol yield of 300 L/ton wood and ethanol high heating value of 24 MJ/L. Because mechanical-electric energy used for wood size reduction is converted from chemical or thermal energy (stored in ethanol) with efficiency of approximately 30%, the thermal energy in ethanol produced is just sufficient for wood-size reduction. This poses a significant challenge in bioconversion of biomass with strong physical integrity such as wood, giant reed, and bamboo, etc. We proposed and demonstrated a post-pretreatment size reduction approach at the USFS Forest Products Laboratory to significantly reduce mechanical energy consumption for wood size reduction through disk milling [24,115,116]. Pretreatment removed portions of the wood solid and loosened the wood structure to reduce energy for size reduction. Energy consumption for disk-milling lodgepole pine wood chips was reduced by as much as approximately 80%, while achieving over 90% enzymatic cellulose conversion of the resultant substrate, when pretreated by SPORL at approximately pH = 2 [116]. Similar levels of reduction in milling energy for dilute acid pretreated wood chips was also achieved [116]. Energy savings from disk milling using this post-pretreatment approach of lodgepole pine pretreated by different processes are shown in Fig. 3. The results indicate that energy savings is significantly affected by the pretreatment process applied. In general, a low pH pretreatment process, such as SPORL at pH = 1.9 and dilute acid (pH = 1.1 [116]) produced more energy savings than a high pH pretreatment. This is probably due to the strong degradation of carbohydrates by acid hydrolysis, which was clearly seen from the morphologies of resultant solid substrates using SEM imaging [116]. The application of sulfite further facilitates disk milling to save energy. It is expected that energy savings from alkaline pretreated materials will be less than that achieved from acid based pretreatments based on the results shown in Fig. 3. The post-chemical pretreatment size reduction approach has the benefits of (1) avoiding the difficult process for separating pretreated solids, and (2) eliminating mixing required for aqueous pretreatment of fiberized materials [19,115].

Thermal energy for thermo-chemical/physical pretreatment at elevated temperatures is another major energy input which mainly depends on two factors: the pretreatment temperature and solids loading or liquid to solids ratio (L/S). Steam pretreatment has additional energy cost, i.e., the latent heat of steam. Reducing L/S ratio is critical to reduce pretreatment energy because the thermal

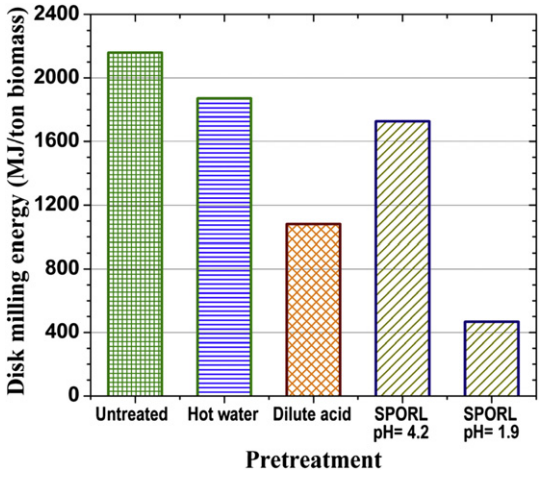

Fig. 3. Effects of pretreatment on energy consumption for disk milling of wood chips using post-pretreatment wood size reduction approach at disk-plate gap of 0.76 mm and solids discharge consistency of 20%. Data from Zhu et al. [116].

energy consumption for pretreatment is almost linearly proportional to L/S based on thermodynamic calculations [115]. To further illustrate this point, the thermal energy required to heat biomass suspensions of different solids to 150, 170, and 190 °C was calculated as shown in Fig. 4. The results indicate that thermal energy for pretreatment rapidly increases as solids loading decreases. The slopes of the curves suggest that a critical minimum solids loading of 25% or higher is required to achieve significant reduction in thermal energy input for pretreatment. Reducing pretreatment temperature has much less effect than increasing solids loading for reducing thermal energy input. This is especially true at high solids loadings of 40% or higher. Reported studies on ionic liquid pretreatment used low consistencies (or large L/S) that resulted in high energy input even under low pretreatment temperatures; for example, Thermo-energy input for pretreatment is above 6750 MJ/ton biomass for three literature studies using L/S = 20 at 80 °C [152], L/S = 20 at 90 °C [130], and L/S > 15 at 105 °C [129].

Enzymatic saccharification efficiency of a given lignocellulosic feedstock can be improved at the expense of energy cost through a more severe pretreatment by increasing both temperature and degree of size reduction. Therefore, it is necessary to define a pretreatment energy efficiency to quantitatively compare different pretreatment processes [83,115], where total sugar recovery yield is the total sugar recovery as a fraction of total biomass sugar (theoretical sugar yield). Energy consumption for pretreatment should include both thermal energy input and energy for biomass size reduction. The energy for producing the chemicals used in pretreatment should also be included. Ideally, the energy for producing the enzymes for hydrolysis as well as the mixing energy for enzymatic saccharification should also be included especially when comparing substrates using different enzyme loadings. Both total sugar recovery and pretreatment energy efficiency should be used in evaluating and comparing the performance of pretreatment processes [19,117].

$$\eta_{\text{Pretreatment}} = \frac{\text{Total sugar recovery yield (\%)}}{\text{Total energy consumption for pretreatment}} \quad (1)$$

3.4.2. Energy input for enzymatic saccharification and fermentation

Mixing of aqueous lignocelluloses at high solids for enzymatic saccharification and fermentation can be energy intensive. Unfortunately, data on mixing energy for high solids enzymatic saccharification are almost nonexistent. There are only a few laboratory q-SSF studies that reported mixing energy data [83,139].

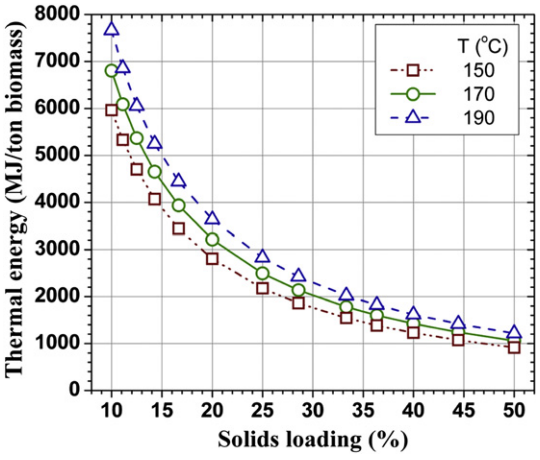

Fig. 4. Effect of lignocelluloses solids loading on thermal energy required for aqueous thermo-chemical pretreatment.

These studies indicated that liquefaction can take place rapidly when the substrate is properly pretreated. However, mixing energy increased rapidly as solids loading is increased [139]. It was found that mixing energy using the ribbon mixer was raised from 570 to 1350, and to 3360 MJ/ton when solids loading of a steam exploded corn stover was increased from 20, to 25, and to 30% [139], respectively. The energy input of 3360 MJ/ton is almost the total thermal energy of the ethanol produced from the corn stover. Mixing energy using a torque rheometer reported in our own study was only 160 and 290 MJ/ton for SPORL and dilute acid pretreated aspen substrates saccharified at 18% solids [83]. Although these studies were produced at laboratory scales, they suggest that mixing energy is on the order of 500 MJ/ton biomass at moderate solids loadings of approximately 20%. Furthermore, combining a high shear mixing for a short period of time for rapid lignocellulose liquefaction with a subsequent low intensity mixing is probably a good strategy to reduce mixing energy.

3.4.3. Energy input for downstream separation and processing

Separation of ethanol from water is often accomplished by distillation to the ethanol azeotrope concentration in water of approximately 95% followed by dehydration [153]. Distillation energy can be estimated from fundamental thermodynamic calculations. This type of calculation indicates that distillation energy decreased rapidly as ethanol titer increases (http://www.ces.purdue.edu/extmedia/ae/ae-117.html). For example, distillation energy can be reduced from approximately 19,000 to 6000 MJ/ton ethanol when ethanol titer is increased from 2 to 7 wt%. The savings in the distillation energy diminished with further increase in ethanol titer. The number of 6000 MJ/ton is close to the 6300 MJ/ton measured at a farm scale ethanol distillation system which accounted for product condensation and thermal energy losses [154]. The energy input for dehydration of ethanol vapor is mainly for the recovery of sorbent. When cornmeal or cellulosic sorbents were used, the energy to regenerate the adsorbent for dehydrating ethanol of 92.6% concentration was approximately 528 MJ/ton ethanol [153], or less than 10% of the distillation energy. Assuming ethanol yield of 300 L/ton biomass, the distillation and dehydrating energy can be estimated to be 1600 MJ/ton biomass using the average distillation and dehydrating energy of 6500 MJ/ton ethanol.

3.4.4. Analysis of literature data on biorefinery operations

Limited literature reported complete process mass and energy balance for biorefinery operations despite so much biorefinery related research has been published in the last 2 decades. Table 4 summarizes 11 studies from the retrievable literature that represent the state of art of cellulosic ethanol production concepts using different pretreatment processes. It should be pointed out that the studies conducted by the National Renewable Energy Laboratory (NREL) and Kazi et al. [10,13] are not a single complete study, rather summaries of potentially achievable scenarios based on numerous separate studies over a period of time. Recently NREL adopted a low temperature (158 °C) dilute acid pretreatment process for corn stover, however, the reported ethanol production was based on pretreatment conducted at 190 °C [10].

To provide a complete picture about the net energy aspects of these studies and their pretreatment process technology concepts, the biomass type and feedstock physical-size used in pretreatment are also listed whenever available. The energy consumptions for feedstock size reduction were not reported and were estimated based on literature data [149]. Wood chipping energy of 180 MJ/ton were estimated based on pulp mill experience [155] and was used for the three woody biomass studies [28,50,83]. The reported disk milling energy of pretreated wood chips were added to the wood chipping energy to obtain total wood size reduction energy for the

Table 4
Literature data on biorefinery operation and energy input in MJ/ton biomass.

	Kazi et al. [13]	NREL [10]	Oberoi [158]	Jin et al. [85]	Jin et al. [86]	Ko et al. [156]	Nieves et al. [87]	Nieves et al. [82]	Monavari et al. [28],	Zhu et al. [83]	Tian et al. [50]
Biomass	Corn stover	Corn stover	Rice straw	Switchgrass	Corn stover	Rice straw	Sugarcane bagasse		Spruce	Aspen	Lodgepole pine
Biomass size	Particles: < 6.4 mm	Particles: < 6.4 mm	Particles: 0.6 mm			Particles 0.4–0.7 mm	Particles <3 mm: 10% > 50 mm:10%; 3–25 and 25–50 mm: 80%		Particles 2–10 mm	Chips 6–38 mm	Chips 6–38 mm
Size reduction energy	**20**	**20**	**200**	**20**	**20**	**200**	**20**		**360**	**370**	**940**
Pretreatment method	Hot-water	Dilute sulfuric Acid		AFEX	AFEX	Aqueous Ammonia	Phosphoric acid steam explosion		SO_2 Steam Explosion	SPORL	SPORL
Energy for chemicals[a]		**413**	**241**	**687**	**343**	**505**	**128**		**~30**	**~60**	**~100**
Acid (kg/ton biomass)		24	219				10			11	22
SO_2 or $NaHSO_3$ (kg/ton biomass)									35	30 ($NaHSO_3$)	80 ($NaHSO_3$)
Ammonia (kg/ton biomass)		11.4		2000	1000	1470					
Pretreatment energy	**1618**	**2158**	**5210**	**2286**	**1857**	**2330**	**3345**		**4348**	**2496**	**2661**
Pretreatment T (C°)	190	190	132	140	140	70	180		200	170	180
Pretreatment solids (%)	40	30	10	50	40	14.3	50		41.7	25	25
Energy for enzymes	**282**	**282**	**372**	**647**	**550**	**250**	**351**	**619**	**504**	**184**	**435**
Enzyme dosage (kg protein/ton biomass)	10.6	10.6	14.0	24.4	20.7	9.4	13.2	23.3	19.0	7.0	16.4
Ethanol titer (g/L)		54	21	36	39	12	20	27		59[b]	21
Ethanol yield (L/ton)	211	~280	253	241	307	152	253	342	301	211 + ~56[c]	270
Total energy input	**1901**	**2855**	**6022**	**3640**	**2770**	**3285**	**3516**	**3785**	**5179**	**3110**	**4136**

[a] Energy input for sulfuric and phosphoric acid production were from Lou et al. [71] and GREET, respectively. Energy input for ammonia was from GREET with the assumption of 90% recovery of the amount of ammonia applied in three ammonia pretreatment studies. Data with ~ were estimated for two reasons: actual SO_2 dosage were not available from [28]. SPORL can be carried out using SO_2 plus hydroxide, rather than sulfuric acid + $NaHSO_3$.

[b] Fermentation of hemicelluloses stream were not carried out. Ethanol titer of 59 g/L was from the cellulosic solids fraction.

[c] Ethanol production from hemicellulosic sugar stream was estimated to be 56 L/ton based on reported sugar yield with 70% fermentation efficiency.

two SPORL studies [50,83]. Energy inputs for producing pretreatment chemicals were calculated from sources as indicated and the reported chemical dosages in the Table. A 90% of recovery of ammonia was assumed for the three ammonia pretreatment studies [85,86,156]. Thermal energy input for pretreatment was determined based on thermodynamic calculations of pulp suspension using the reported pretreatment temperature and consistency or liquid to solid ratio (L/S). For the two AFEX and the aqueous ammonia studies [85,86,156], the enthalpy of ammonia at the pretreatment temperature was estimated from literature specific heat values [157] and added to the thermal energy input. This is because of the high ammonia loadings and the significant amounts of energy required to heat the ammonia to the pretreatment temperature in these three studies. The energy consumption for enzyme production was also estimated based on the reported enzyme dosage and reported energy input for enzyme production in a cellulosic ethanol study using corn stover [71]. Energy inputs for other processes, such as mixing for enzymatic saccharification and fermentation, ethanol distillation, waste water treatment, energy for equipment were not reported in these studies.

Several observations can be made from the 11 studies listed in Table 4. Thermal energy input is the most energy intensive step. Increasing pretreatment solids loading is most critical to reduce pretreatment thermal energy input as discussed previously (Fig. 4). The study of Oberoi used a very low solids loading of 10% and therefore required a significant amount of energy input of over 5000 MJ/ton biomass [158]. Steam explosion pretreatment is energy intensive because of the latent heat despite high solids loading [28]. Reducing pretreatment temperature can reduce thermal energy input as shown by the two SPORL studies [50,83]; however, the energy savings are not significant unless the reduction in pretreatment temperature is more than 20 °C (Fig. 4). Ammonia based pretreatments used a relatively low pretreatment temperature, however, the very high ammonia loading and specific heat of ammonia significantly offset the savings from low temperature pretreatment.

Energy input for biomass size reduction can be important. This is especially true for woody biomass. Both steam explosion using small wood particles [28] and post SPORL pretreatment disk milling [50,83] are effective to reduce energy consumption for wood size reduction while achieving good biomass bioconversion.

Energy input for enzyme production can be significant. Low to moderate enzyme loadings are preferred. However, a more severe pretreatment is often required when a low enzyme loading is used for a given pretreatment process without affecting enzymatic cellulose saccharification efficiency. Advanced enzyme formulation has shown promise to reduce enzyme loading without severe pretreatment and affecting cellulose conversion efficiency as demonstrated recently by NREL.

Energy input for pretreatment chemical production is low in most cases without the recycling of the chemicals. However, high efficiency in recycling of chemicals is required for AFEX pretreatment because of the high ammonia applications on the order of 100% on biomass. The energy input for ammonia production listed in Table 4 for the two AFEX and the aqueous ammonia runs [85,86,156] were estimated with the assumption of 90% ammonia recovery. The key to reduce energy input for ammonia based pretreatment is to reduce ammonia application and improve ammonia recovery efficiency.

Energy input (including biomass size reduction) for steam explosion pretreatments are higher than that for aqueous pretreatment. This is especially true when a high solids loading is used in aqueous pretreatment [10] and steam explosion is applied to nonwoody biomass (comparing [10] with [82,87]). Steam explosion can be competitive to aqueous pretreatment in terms of energy input to pretreat woody biomass (comparing [28] with [50,83]), especially when recovery of heat is adopted.

Finally, the results in Table 4 also suggest that woody biomass can be processed to produce biofuel through a biorefinery as efficiently as herbaceous biomass and agricultural residues when proper pretreatment technologies are employed. Suitability of local landscape, biomass agricultural operation and productivity, harvesting, storage, and logistics should be weighted significantly more heavily than biomass processing in determining which biomass should be used as the right feedstock for a given biorefinery.

We can use two levels of energy input for biorefinery operations of herbaceous biomass at 2300 and 4000 MJ/ton biomass, respectively, as well as two levels of energy input at 2500 and 4500 MJ/ton biomass for woody biomass, respectively. This two level analysis represents a sensitivity study. When pretreatment solids loading is increased to 40% (achievable based on Kazi et al. [13]), the energy input used in the NREL study [10] can be reduced to approximately 2300 MJ/ton that included energy for ammonia used to neutralize pretreatment hydrolysate. So, 2300 MJ/ton is used as the most optimistic energy input for biorefinery operation using herbaceous biomass. 4000 MJ/ton represents the highest energy input using herbaceous biomass listed in Table 4. When the pretreatment solids loading is increased to 33% (achievable based on our laboratory study without sacrificing cellulose conversion) from 25% used in the study of Zhu et al. [83], the pretreatment thermal energy can be reduced by 600 MJ/ton or more (Fig. 4). Therefore total energy input for the study of Zhu et al. [83] listed in Table 4 can be reduced to 2500 MJ/ton that is used for the optimistic estimates of energy inputs for woody biomass. Because approximately 84% of the energy input for the study of Monavari et al. [28] was for steam production and a significant fraction is recoverable, 4500 MJ/ton that represents the average energy input for the study of Monavari et al. [28] and Tian et al. [50] is used as the conservative estimate for woody biomass. Energy input of 500 MJ/ton for the operation of enzymatic saccharification and fermentation (excluding enzyme production) is estimated based on the laboratory high solids studies [83,139] as discussed in Section 3.4.2. Energy input of 1600 MJ/ton biomass for distillation and separation is based the discussions in Section 3.4.3. Additional energy inputs labeled as “other biorefinery” in Table 5 including waste water treatment, capital equipment, and water usage are added based on the data reported by the EBAMM Model [78]. Potential thermal energy recovery of the energy input for thermo-chemical pretreatment is not taken into account considering there are other energy inputs unaccounted for, such as for heating and air conditioning for plant and office buildings, numerous pumps and other auxiliary equipment used in the plant.

4. Overall energy balance analysis

Based on the discussions of the three scenarios of energy input for agriculture operation outlined in section 3.2.2, we can create 5 scenarios for analyzing overall energy balance for biofuel production from lignocellulosic biomass as listed in Table 5. Each scenario has two levels of energy input for biorefinery operations as discussed above in section 3.4.4. Net energy productions were calculated with and without energy from lignin. Except for the scenario of corn stover with the major product corn given a credit of over 25,000 MJ/ton corn stover [71], the most conservative estimate with high level of energy input for major biorefinery operation resulted in a net energy output from ethanol (HHV base) approximately −500–200 MJ/ton biomass. The most optimistic estimate with low level of energy input for biorefinery operation resulted in a positive energy output of approximately 2000 MJ/ton biomass.

Table 5
Analyses of net energy production (MJ/ton biomass) from lignocellulosic biomass through biochemical conversion.

Energy input	Woody biomass						Agriculture residues						Nonwoody energy crops			
	Forest harvest residues as waste			Woody energy crops			Corn stover or straw as waste			Stover or straw with corn or rice or wheat			Switchgrass, etc			
Agriculture (MJ/ha)[a]	4936 (I)			7660 (III)			2094 (I)			18094 (II)			4697 (III)			
Major product credit	0			0			0			25560[h]			0			
Biomass transportation[b]	59			59			177			177			177			
Biorefinery	2500	–	4500	2500	–	4500	2300	–	4000	2300	–	4000	2300	–	4000	
High solids enzymatic saccharification and fermentation	500			500			500			500			500			
Distillation and separation	1600			1600			1600			1600			1600			
Other biorefinery[c]	250			250			250			250			250			
Total energy input	**5526**	–	**7526**	**5675**	–	**7675**	**5229**	–	**6929**	**8299**	–	**9999**	**5389**	–	**7089**	
Co-product credit[d]	123			123			123			123			123			
Lignin energy[e]	5320			5320			3990			3990			3990			
Ethanol energy[f]	7030			7030			7030			7030			7030			
Net energy	**6947**	–	**4947**	**6798**	–	**4798**	**5914**	–	**4214**	**28404**	–	**26704**	**5754**	–	**4054**	
Net energy from ethanol alone	**1627**	–	**−373**	**1478**	–	**−522**	**1924**	–	**224**	**22414**	–	**24714**	**1764**	–	**64**	
Biomass yield (kg/ha/yr)[g]	8000			10000			5212			5212 + 8687 (corn)			8360			

[a] The Roman letter is the scenario number discussed in Section 3.2.2. Harvest residue with 50% replacement of lost nutrients due to harvesting of residues [109]; Detailed explanation of the numbers can be found in the last three paragraphs in section 3.2.2.
[b] The average of EBAMM spreadsheet of Farrell [78]. The packing density of woody biomass is assumed three times of that herbaceous biomass.
[c] Included process water, effluent restoration, capital equipment. Based on average of EBAMM spreadsheet of Farrell [78].
[d] Based on average of EBAMM spreadsheet of Farrell [78].
[e] Assuming available lignin content of 20 and 15% for woody and herbaceous biomass, respectively. Lignin HHV $= 26.6 \times 10^3$ MJ/ton.
[f] Assuming ethanol yield 300 L/ton, ethanol HHV $= 29.7 \times 10^3$ MJ/ton.
[g] Forest harvesting residues based on Whittaker et al. [110]; Corn stover based on Luo et al. [71]; Woody energy crops based on Zalesny et al. [163]; Switchgrass based on average of Schmer et al. [77].
[h] Based on Luo et al. [71].

When lignin energy is included, net energy production is apparent, from approximately 4000–7000 MJ/ton biomass. This suggests that a ratio of net energy output over energy input of approximately 1:1. This ratio is much lower than that in petroleum production, a major concern in production of energy from corn and lignocelluloses [159].

The data shown in Tables 4 and 5 suggest that energy input for pretreatment is most significant and needs to be reduced to improve energy efficiency. In the near term this can be achieved by improving solids loading in pretreatment [115] as shown in Fig. 4. The low pretreatment energy input in the studies of Kazi et al. [13] is simply because of high solids loading of 40%. Unpublished results in our laboratory indicate that a wood chip solids loading of 40% (L/S = 1.5) can be carried out with little effect on enzymatic cellulose saccharification efficiency and overall sugar recovery using lodgepole pine. Pretreatment energy input can be reduced to approximately 1500 MJ/ton biomass at 40% solids loading or by 40% compared with those at 25% solids loading listed in Table 5 [50,83]. Developing advanced enzyme technologies in the future that require less severe pretreatment may allow lower temperature pretreatment to further reduce pretreatment energy input. The results in Table 5 also indicate that distillation and separation is another energy intensive step. Increasing ethanol titer to 6% is necessary to improve overall biofuel production energy efficiency. Significant reduction of this energy input is possible in the future by further increasing ethanol titer and developing membrane separation technologies [146–148] or producing non-alcohol biofuels. Improved substrate enzymatic digestibility can reduce cellulase loading leading to reduced energy input for cellulase production. The results in Table 4 suggest that cellulase loading varied significantly among different studies using different lignocellulosic biomass. The differences in net energy production from woody versus herbaceous biomass and agricultural residues are negligible when proper pretreatment technologies are used for woody biomass. The study using aspen wood chips demonstrated the effectiveness of SPORL process to achieve high ethanol yield and titer at low cellulase loadings [83].

5. Conclusions

This review presented a detailed analysis of energy inputs and outputs from biomass biorefinery operations along with energy inputs from agriculture operations based on published literature data. The data indicate that energy inputs for fertilizer and farm machinery production, and fuels for farming operations are the three highest energy uses of energy for agricultural operation. It was found that major discrepancies exist in the reported data on energy inputs for fertilizer production and fuels for farms. This is because existing literature allocated these two energy inputs all to corn stover and nothing to corn, the major product in corn farming. The data collected on switchgrass farms revealed much lower energy input for both fertilizer production and fuel for farming. Proper allocation of certain energy inputs for corn farming between corn and corn stover or better estimate of energy credits from corn are critical to provide accurate estimate of net energy output from corn stover. The discrepancy in energy input for farm machinery among literature studies is as large as by over 25 folds. The group holds negative position towards biomass for bioenergy used a significantly high (as much as 25 folds or more) energy input to make it the second largest energy input in agriculture operation. This suggests experimental study is needed to provide a better estimate. The proper dosage of re-fertilization to replace the loss of nutrients due to harvesting residues in forest plantations needs to be investigated to better quantify energy input for collecting forest residues. More studies are also needed to better estimate energy input for the production of woody energy crops.

Energy input for thermo-chemical pretreatment is the most energy intensive step in a biorefinery operation. Increased pretreatment solids loading is the most effective approach to reduce this energy input. A minimal critical solids loading of 25% is

required to significantly reduce thermal energy input for thermochemical pretreatment. Energy consumption for woody biomass size reduction can also be energy intensive. The post-thermochemical pretreatment wood size reduction approach can effectively reduce this energy input and should be adopted. Energy input for pretreatment chemicals are low for most pretreatment technologies except for ammonia based pretreatment suggesting high ammonia recovery efficiency is required to significantly reduce energy input. Energy input for downstream distillation or separation is another energy intensive step especially for producing alcohol based biofuel. Increasing biofuel titer and developing advanced membrane separation technologies or non-alcohol based biofuel are potential avenues to reduce this energy input. Energy inputs for enzyme production can be high at high cellulase loadings and can be reduced by using more robust pretreatment processes.

The optimistic estimate of net energy production of approximately 2000 MJ/ton biomass from ethanol alone (HHV base), or approximately 7000 MJ/ton biomass from ethanol and lignin is achievable with total energy input on average of approximately between 6000 and 8000 MJ/ton. Therefore, in terms of energy input over net energy output, energy production from bioconversion of lignocelluloses is not very efficient. Future development in enzyme and biofuel separation technologies would allow for further reduction in pretreatment and downstream separation energy consumptions to improve energy efficiency.

Woody biomass with high lignin content tends to produce more net energy when energy from lignin is included. Despite the strong recalcitrance of woody biomass, it can be processed as efficiently as herbaceous biomass and agricultural residues for biofuel production when using proper pretreatment technologies. The advantages of woody biomass in transportation and logistics should not be overlooked.

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