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Short Communication

Evaluation of electricity generation from lignin residue and biogas in cellulosic ethanol production

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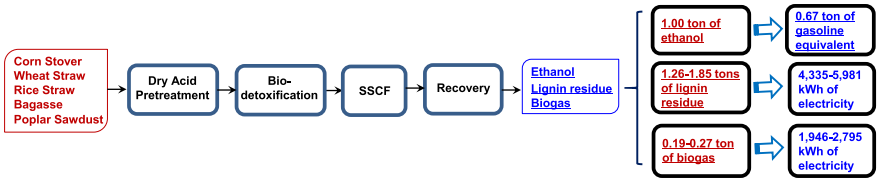
HIGHLIGHTS

- Mass balance of cellulosic ethanol production from five feedstocks was established.
- HHV of lignin residue, COD and BOD_5 of wastewater were measured.
- Electricity generation from lignin residue and biogas was calculated and analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

This study takes the first insight on the rigorous evaluation of electricity generation based on the experimentally measured higher heating value (HHV) of lignin residue, as well as the chemical oxygen demand (COD) and biological oxygen demand (BOD_5) of wastewater. For producing one metric ton of ethanol fuel from five typical lignocellulose substrates, including corn stover, wheat straw, rice straw, sugarcane bagasse and poplar sawdust, 1.26–1.85 tons of dry lignin residue is generated from biorefining process and 0.19–0.27 tons of biogas is generated from anaerobic digestion of wastewater, equivalent to 4335–5981 kWh and 1946–2795 kWh of electricity by combustion of the generated lignin residue and biogas, respectively. The electricity generation not only sufficiently meets the electricity needs of process requirement, but also generates more than half of electricity surplus selling to the grid.

1. Introduction

Lignocellulose biomass is the most important feedstock option to compete with starch and sugar feedstock for production of biofuels and bulk chemicals (Wyman and Dale, 2015). Currently, the lignocellulose biorefining technology is in the developing stage. The energy and water balance is obviously unfavorable to that of the mature corn ethanol production in consuming more fresh water, steam, electricity (McAloon et al., 2000; Aden, 2007; Balan, 2014), and generating more wastewater (Wingren et al., 2008; Sassner and Zacchi, 2008b; Martin and Grossmann, 2011). Lignocellulose biorefining also lacks opportunity to recover costs from high added value byproducts that may be available with other substrates such as distillers dried grains with soluble (DDGS) from corn fermentation. On the other hand, lignin residue generation adds a high credit of electricity to the cellulosic ethanol production by combustion of lignin residue after cellulose and hemicellulose are converted into ethanol (Humbird et al., 2011). Biogas (methane) from the anaerobic digestion of wastewater from ethanol distillation provides an additional gas fuel for electricity generation (Humbird et al., 2011). The electricity generation credit could balance the electricity consumption in cellulosic ethanol production process and also sell the surplus electricity to grid.

In biorefining process, cellulose and hemicellulose in lignocellulose feedstock are enzymatically hydrolyzed into fermentable sugars and then fermented into ethanol or biochemicals, while the lignin portion is left behind as solid residue after ethanol is distillated and water is filtrated from the residue. The higher heating value (HHV) of the pure lignin is 26.7 GJ per metric ton, which is competitive or even better than the raw coal (20.9 GJ/ton) (Achambault-leger et al., 2015). The practical lignin residue

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contains unconverted cellulose and hemicellulose, fermenting microorganisms and inert solids, but its heating value is still high enough to be used as boiler fuel. Wastewater is generated from the distillation of ethanol fermentation broth followed by a liquid-solid filtration. The wastewater is anaerobically and aerobically digested to remove the chemicals indicated by chemical oxygen demand (COD) value and generate biogas. Both the biogas and the sludge cake are capable of combustion use for electricity generation in a combined heat and electricity facility.

Although the lignin residue and biogas demonstrated great potentials for electricity generation, the previous studies did not deliver the rigorous evaluation based on the experimentally measured data of practical lignin residues or biogas. For lignin residue, only the HHV value of pure lignin component was applied for evaluation of electricity generation, instead of the experimentally measured heat values using the practical lignin residues, the practical lignocellulose feedstocks, and the practical processing of cellulosic ethanol production (Cardona and Sanchez, 2006; Achambault-leger et al., 2015). For biogas, the COD and BOD data were rarely experimentally measured and usually the rough estimation was made based on the limited COD data (Steinwinder et al., 2011; Humbird et al., 2011).

In this study, the cellulosic ethanol production from five typical lignocellulose biomass including corn stover, wheat straw, rice straw, sugarcane bagasse and poplar sawdust was performed by dry acid pretreatment and biodetoxification (DryPB), followed by a high solids loading simultaneous saccharification and co-fermentation (SSCF) to achieve the high ethanol conversion efficiency (approximately 11% of ethanol titer by volumetric percentage in the fermentation broth). The mass balance of cellulosic ethanol production was calculated as the basis of electricity generation calculation. The higher heating values (HHV) of the lignin residues, the COD and BOD_5 values of the wastewater from the distillation stillage from the five representative lignocellulose feedstocks were experimentally measured according to the standard methods. Based on these data, the electricity generation from lignin residue and biogas were rigorously calculated and analyzed. This study took the first insight on the rigorous evaluation of electricity generation in cellulosic ethanol production. The results provided the important data for designing of commercial scale cellulosic ethanol plant and evaluating cellulosic ethanol economy.

2. Materials and methods

2.1. Raw materials

Five lignocellulose feedstocks were collected from their dominant growing regions in China. Corn stover was harvested from Bayan Nur, Inner Mongolia, China in fall 2015. Wheat straw was harvested from Dan Cheng, Henan, China in fall 2013. Rice straw was harvested from Chang Zhou, Jiangsu, China in fall 2014. Sugarcane bagasse was obtained from the sugar plant of Bei Hai, Guangxi, China in fall 2014. Italian poplar sawdust was obtained from the wood factory in Yan Cheng, Jiangsu, China in fall 2015. The field dirt, sands, metal pieces and other impurities were carefully avoided during the collection and then screened during the prehandling. The collected corn stover, wheat straw, rice straw and sugarcane bagasse were ground coarsely using a beater pulverizer and screened through a mesh with the circle diameter of 10 mm. Poplar sawdust was used directly without grinding.

The composition of the lignocellulose feedstocks was measured by the two-step acid hydrolysis method according to National Renewable Energy Laboratory (NREL) protocols (Sluiter et al., 2008, 2011). On the dry weight base (w/w), corn stover contained 35.4% of cellulose, 24.6% of hemicellulose, 16.1% of lignin, and 3.5% of ash; wheat straw contained 38.7% of cellulose, 25.9% of hemicellulose, 14.9% of lignin, and 5.2% of ash; rice straw contained 35.3% of cellulose, 18.4% of hemicellulose, 22.5% of lignin, and 9.3% of ash; sugarcane bagasse contained 38.8% of cellulose, 23.9% of hemicellulose, 26.4% of lignin, and 1.3% of ash; poplar sawdust contained 39.7% of cellulose, 16.6% of hemicellulose, 29.4% of lignin, and 3.2% of ash.

2.2. Dry acid pretreatment and biodetoxification (DryPB) biorefining process

Ground lignocellulosic biomass is pretreated using the dry acid pretreatment method at 175 °C for 5 min with 2.0 g sulfuric acid per 100 g dry biomass in the 20 L pretreatment reactor (Zhang et al., 2011; He et al., 2014a,b). All the dilute acid solution and the condensed water were completely adsorbed into the solids to form approximately 50% (w/w) of the dry pretreated feedstock solids with the pH around 2.0, and no free wastewater stream was generated. The sulfuric acid in the pretreated biomass solids was neutralized to 5.5 by the addition of 20% (w/w) $Ca(OH)_2$ suspension slurry. The pretreated biomass solids were briefly milled by a disk milling machine (PSB-80JX, Fleck Co., Nantong, Jiangsu, China) to remove the extra-long fibers to avoid the blockage of pipelines and valves in the downstream flow of the hydrolysate slurry and broth.

Then the pretreated solids were aerobically biodetoxified using *Amorphotheca resinae* ZN1 in a 15 L bioreactor to remove the inhibitors generated during the dry acid pretreatment operation at 28 °C the water saturated aeration of 0.8 vvm for 36–48 h (Zhang et al., 2010a; He et al., 2016). The major inhibitors were completely assimilated and degraded. Xylose and glucose released during the pretreatment were preserved without observable loss. And no cellulose degradation was observed during the biodetoxification period.

The pretreated and biodetoxified lignocellulose feedstock solids were enzymatically hydrolyzed into liquid hydrolysate slurry containing both mono and oligomer sugars in the specially designed 5 L bioreactors equipped with helical ribbon impeller at 50 °C, pH 4.8 and 150 rpm for 12 h (Zhang et al., 2010b). Then glucose and xylose were co-fermented into ethanol simultaneously with the hydrolysis of cellulose and oligomer sugars at high solids loading (30%, w/w) and low cellulase dosage (10 mg protein/g cellulose) at 30 °C for 96 h by inoculating the shortly adapted yeast seed cells *S. cerevisiae* XH7 into the hydrolysate at 10% (v/v). pH was maintained at 5.5 by adding 5 M NaOH solution.

Fermentation broth from corn stover, wheat straw, rice straw, sugarcane bagasse, or poplar sawdust was directly distillated to recover ethanol to about 35% (w/w) distillate in a glass distillation equipment with the inner column diameter of 40 mm filling with stainless theta ring packings (3 mm in diameter). The stillage from the distillation column was filtrated by a press filter machine through a fabric cloth to yield the wastewater stream and the lignin residue cake.

2.3. Determination of higher heating value, COD and BOD_5

Lignin residue cake with the thickness of 4 mm contained approximately 65% (w/w) of dry solids. It was dried at 105 °C until constant weight and sent for determination of higher heating value on a calorimeter (MMC 274 multi-module, Netzsch Co., Fresitaat Bayerm, Germany) according to the China National Standard Method GB/T213-2003 (Determination of Calorific Value of Coal).

The wastewater stream was sent for determination of chemical oxygen demand (COD) and biochemical oxygen demand after 5 days (BOD_5). The COD of the wastewater was determined according to the China National Environmental Protection Standard

Method HJ/T399-2007 (Water Quality Series, Determination of Chemical Oxygen Demand, COD). Briefly, the oxidation was carried out at 165 °C for 15 min in a digester (Hach DRB200, Hach Inc, NY, USA) and the absorbance was measured at 600 nm on a spectrophotometer (Hach DR5000, Hach Inc, NY, USA). Potassium dichromate was used as oxidizing agent and potassium biphthalate was the control. The BOD_5 of the wastewater from the same source was determined according to the China National Environmental Protection Standard Method HJ505-2009 (Water Quality Series, Determination of Biochemical Oxygen Demand after 5 Days, BOD_5). Briefly, the wastewater was cultured at 20 °C for 5 days in glass bottles in an anaerobic flask inoculated with the standard microbe seed and then the dissolved oxygen consumption was determined.

3. Results and discussion

3.1. Mass balance in cellulosic ethanol production

Corn stover, wheat straw, rice straw, sugarcane bagasse, and poplar sawdust were dry acid pretreated and biodetoxified to yield the inhibitor free and high xylose containing feedstock for simultaneous saccharification and co-fermentation (SSCF). SSCF from the five feedstocks achieved high ethanol titer of 85.1, 87.0, 71.9, 78.3, and 79.1 g/L (9.1–11.0% in volumetric percentage), respectively (Liu et al., 2017). Ethanol in the fermentation broth was distillated. The mixed lignin residue and wastewater slurry was recovered as the bottom stream of the distillation column. The slurry was filtrated to get the lignin residue cake and wastewater liquid. The mass balance of biomass, water, ethanol and lignin residue in the biorefining process was calculated based on the experiment results (Fig. 1). Processing one metric ton lignocellulosic feedstocks, ethanol yield is 0.215–0.260 ton, in which the highest one is 0.260 ton ethanol per ton of wheat straw and the lowest is 0.215 ton of ethanol per ton of rice straw, mainly due to the different cellulose and xylan content among the lignocellulose feedstocks. Meanwhile, 0.546–0.658 ton of lignin residue (with the water content of 35%) and 2.204–2.250 tons of wastewater are generated from one metric ton of feedstocks. On the basis of ethanol fuel product, production of one metric ton of ethanol approximately generates 1.26–1.85 tons of dry lignin residue and 8.66–10.27 tons of wastewater.

3.2. Electricity generation form lignin residue

The higher heating values (HHV) of lignin residues were experimentally determined according to the standard methods and the equivalent electricity generation was calculated (Table 1). The HHV values are in the range of 17.12–18.88 GJ per dry ton of lignin residues from corn stover, wheat straw, rice straw, sugarcane bagasse, or poplar sawdust. The HHV values are approximately 70% of the pure lignin (26.7 GJ/ton), and 85% of the raw coal (20.9 GJ/ton), due to the existence of the impurities such as the unreacted cellulose, hemicellulose, residual sugars, inert soil solids and minor amount of fermenting yeast cells and cellulase enzyme proteins.

Production of one metric ton of fuel ethanol generates 1.26–1.85 tons of lignin residues (dry base) according to the mass balance (Fig. 1). Combustion of 1.26–1.85 tons of lignin residue generates 22.95–31.66 GJ of higher heating values. 1 GJ of heating value is equivalent to 277.8 kWh of electricity based on the theoretical energy equivalence. The boiler efficiency (80%) and the generator efficiency (85%) of the turbine shaft conversion to electricity using the lignin residue fuels are cited from Humbird et al. (2011). Therefore, practically 1 GJ of the higher heating value generates $277.8 \times 0.85 \times 0.80 = 188.9$ kWh of electricity, and 22.95–31.66 GJ of higher heating value generates 4335–5981 kWh of electricity. In summary, for producing one metric ton of ethanol fuel, 4335–5981 kWh of electricity is generated by combustion of the correspondingly generated lignin residue.

3.3. Electricity generation form biogas which produced after wastewater treatment

The wastewater was collected after the filtration of the stillage liquid and the chemical oxygen demand (COD) and the biological oxygen demand after 5 days (BOD_5) were experimentally determined (Table 2). The COD values of the wastewater are in the range of 80–137 g/L for the five lignocellulose feedstocks. The BOD_5 values are in the range of 19–44 g/L for the feedstocks. These values are in agreement of the NREL data (87 g/L of COD) (Humbird et al., 2011) and in the general range of fermentation wastewater (50–120 g/L of COD and 20–60 g/L of BOD_5) (Jin and Zhao, 1987). The ratio of COD/BOD_5 is in the range of 0.22–0.39 and fit the general ratio for anaerobic digestion (>0.3) (Steinwinder et al., 2011).

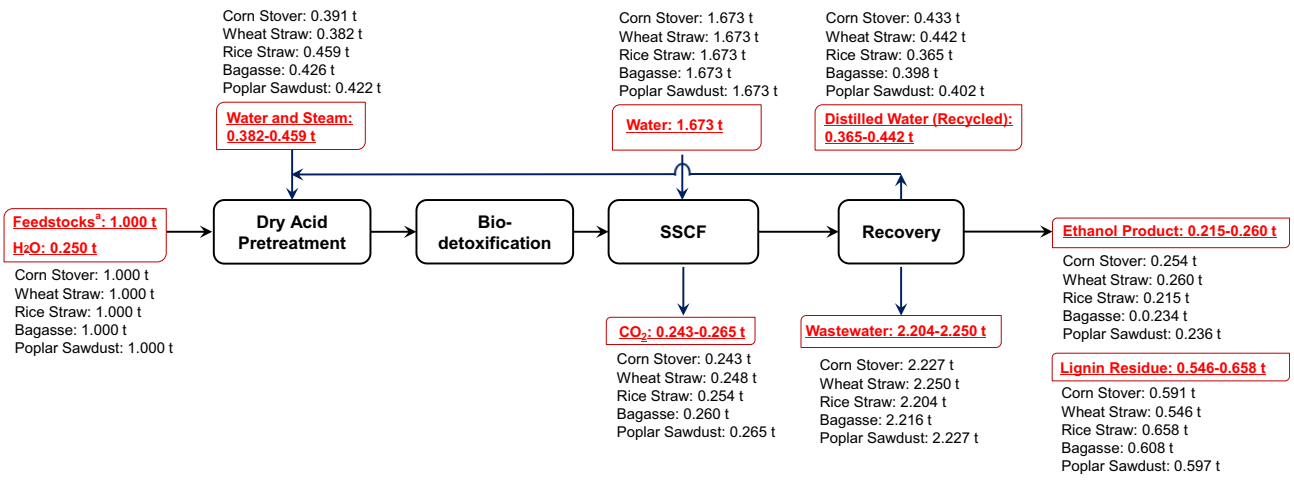

Fig. 1. Mass balance of ethanol production from five lignocellulose feedstocks. [a]One ton of dry lignocellulose feedstock is companied with 0.250 ton of water (20% of water content).

Table 1
Electricity generation from lignin residue combustion.

Feedstock	Lignin residue generation		Higher heating value of lignin residue	Electricity equivalent[a]
	(ton/ton dry solids)	(ton/ton ethanol)	(GJ/ton dry lignin residue)	(kWh/ton ethanol)
Corn stover	0.384	1.51	18.878	5385
Wheat straw	0.355	1.26	18.215	4335
Rice straw	0.428	1.85	17.116	5981
Sugarcane bagasse	0.395	1.57	17.979	5332
Poplar sawdust	0.388	1.52	17.992	5166

[a] Boiler efficiency (80%) for lignin residue or methane combustion and the generator efficiency of the turbine shaft conversion to electricity (85%) were cited from Humbird et al. (2011). 1 GJ of heating value is equivalent to 277.8 kWh of electricity.

Table 2
Electricity generation from biogas combustion after wastewater anaerobic digestion.

Feedstock	Wastewater generation		Chemical oxygen demand (COD) (g/L)	Biological oxygen demand (BOD_5) (g/L)	Methane generation (kg/ton ethanol)	Electricity equivalent[a] (kWh/ton ethanol)
	(ton/ton dry solids)	(ton/ton ethanol)				
Corn stover	2.227	8.768	124	44	267	2795
Wheat straw	2.250	8.664	137	30	266	2786
Rice straw	2.204	10.271	80	29	186	1946
Sugarcane bagasse	2.216	9.481	113	19	242	2538
Poplar sawdust	2.227	9.433	97	38	207	2166

[a] The boiler efficiency of the lignin residue or methane feedstocks (80%) and the generator efficiency of the turbine shaft conversion to electricity (85%) are cited from Humbird et al. (2011). 1 GJ of heating value is equivalent to 277.8 kWh of electricity.

Approximately 0.35 standard cubic meter of biogas or 0.27 kg of methane is obtained from 1 kg of COD removed in the anaerobic digestion of the stillage wastewater (Wingren et al., 2008). Production of one metric ton of ethanol generates 0.19–0.27 ton of biogas according to the mass balance (Fig. 1) resulted from the 91% reduction of the COD in anaerobic digestion (Humbird et al., 2011). Combustion of 0.19–0.27 tons of biogas generates 10.30–14.80 GJ of higher heating values based on the HHV of methane of 55.5 GJ/ton. Similar to lignin residue, 1 GJ of heating value generates 188.9 kWh of electricity, and 10.30–14.80 GJ of higher heating value generates 1946–2795 kWh of electricity. In summary, for producing one metric ton of ethanol fuel, 1946–2795 kWh of electricity is generated by combustion of the correspondingly generated biogas form wastewater.

Combining lignin residue and biogas, the electricity generation from the five typical lignocellulose biomass is in the range of 7121–8180 kWh for producing one ton of ethanol in the present dry acid pretreatment and biodetoxification (DryPB) process. The general energy requirement is 12 GJ of steam (Hinman et al., 1992; Wingren et al., 2008; Piccolo and Bezzo, 2009) and 1306 kWh of electricity (Humbird et al., 2011) for producing one metric ton ethanol. Translating the steam heating into electricity, the total electricity consumption is around 3500 kWh for producing one ton ethanol. Therefore, the electricity generation not only sufficiently meets the electricity need of process requirement, but also generates more than half of the electricity surplus for selling to the grid.

4. Conclusion

Production of one ton of cellulosic ethanol generates 1.26–1.85 tons of dry lignin residue and 0.19–0.27 tons of methane after ethanol recovery from the five typical lignocellulose biomass. The electricity generation from combustion of lignin residue and biogas is in the range of 7121–8180 kWh per ton of ethanol produced in the present DryPB process. The electricity generation sufficiently meets the cellulosic ethanol production needs and generates surplus to the grid.

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