ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg

Research Article

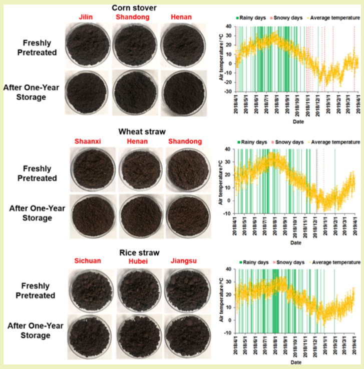
Year-Round Storage Operation of Three Major Agricultural Crop Residue Biomasses by Performing Dry Acid Pretreatment at Regional Collection Depots

Tao Han, Bin Zhang, Hongxing Li, Hongsen Zhang, Yongfu Yang, Lizhen Hu, Xiaodong Ren, Shipeng Wang, Lixiang Zheng, Xushen Han, Gang Liu, Jian Zhang, Qiang Fei, Yueqin Tang, Shihui Yang, Xiaoming Bao, and Jie Bao*

Cite This: https://dx.doi.org/10.1021/acssuschemeng.0c08739

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Commercial cellulosic biofuel operation requires a reliable, low-cost, and stable feedstock logistic system. One great challenge is its long-term storage at least for one harvest cycle (1 year for agricultural crop residues) with a minimum loss of bulky, geographically dispersed, inflammable, and easily degradable lignocellulosic biomass. This study conducted an investigation of year-round storage of the agricultural crop residue feedstock under the scenario of performing dry acid pretreatment at the distributed regional collection depots, instead of the central biorefinery plant. The dry acid pretreatment method provides a practical basis for the storage operation by its ability for high preservation of polysaccharide solids, highly compacted accumulation density, being free from wastewater generation, low capital investment, and low energy consumption. Three major agricultural crop residues (corn stover, wheat straw, and rice straw) were pretreated by dry acid pretreatment and then stored in their major planting regions under varying natural conditions of temperature, rain and snow fall, humidity, wind, and sunlight. The pretreated corn stover, wheat straw, and rice straw contained approximately 50% (w/w) of moisture, and their high water absorption capacity maintained the crop residues in solid and fine-particle forms without free wastewater generation and flammability. Meanwhile, the pretreated crop residues were of low pH value and contained various inhibitory compounds for microbial growth. The results show that the crop residue feedstocks were well preserved with negligible solid and fermentable sugar loss after year-round storage in different regions. The physical properties, chemical compositions, enzymatic hydrolysis yields, and ethanol fermentability were maintained essentially constant with a few positive exceptions such as the increased hydrolysis yield and reduced inhibitor content. A case study shows that the feedstock transportation cost of the long-term stored feedstocks under the scenario of dry acid pretreatment at collection depots was significantly reduced compared to that of the direct transportation of virgin crop residual feedstocks. This study provided an efficient and practical logistic system for large-scale biorefinery plants.

KEYWORDS: *crop residues, year-round storage, lignocellulose, dry acid pretreatment, transportation cost, ethanol*

INTRODUCTION

A reliable, low-cost, and stable feedstock logistic system is the precondition for establishing the commercial-scale cellulosic biobased product industry.[1] Handling and storage of virgin lignocellulose feedstock is one of the major barriers for its commercial operation.[2] One great challenge is its long-term stable storage and transportation with minimum dry matter loss of the bulky, geographically dispersed, inflammable, and easily degradable lignocellulosic biomass at least for one harvest cycle. This means a minimal year-round storage period for agricultural crop residues such as corn stover, wheat straw, and rice straw.[3] The moisture content of freshly harvested lignocellulose feedstocks varies widely (generally from 20 to 45%) depending on the environmental conditions and elapsed time after harvest.[4] Meanwhile, raw crop residues contain water-soluble carbohydrates,[5] which make the crop residues quickly deteriorate. Ensiling and drying are commonly used for preserving agriculture residue lignocellulose feedstocks.[6,7] However, ensilage requires a strictly anaerobic environment in animal forage,[7] and air drying, hot-air drying, or solar drying requires the prolonged period to reduce the water content to 15−20%.[8] The risks of fire and deterioration still exist during these year-round storage period.[9,10] For the feedstock supply chain, the previous analyses further showed that the transportation cost of virgin feedstocks outweighs its reasonable

Received: December 1, 2020
Revised: February 23, 2021

cost share of the biorefinery chain, owing to the low bulk density of the virgin feedstocks, compositional variability, and tendency to deterioration.[2,11−14] Dale and his colleagues proposed a concept of regional biomass processing depots by the decoupling pretreatment operation from central biorefinery plants to scattered biomass collection depots where the loosely bound feedstock is preprocessed and pretreated.[1,3] This new concept demonstrated the advantage of the lignocellulose feedstock storage in its pretreated form, instead of the virgin feedstock.

Pretreatment plays a decisive role in the feasible storage operation of lignocellulose feedstocks at regional collection depots. Pretreatment is a harsh process that disrupts the lignocellulosic structure to release its fermentable sugars.[15,16] The inhibitors generated from pretreatment creates a favorable condition to avoid microbial invasion and carbohydrate deterioration during long-term storage of the lignocellulose feedstock.[17−19] Furthermore, pretreatment at the regional collection depots, usually the rural areas with a weak infrastructure system, requires increased concerns on waste release. Therefore, the pretreatment operated at regional collection depots should generate zero wastewater streams and produce dry solid particles suitable for packing, instead of the wet slurry form.[1] Therefore, the pretreatment methods such as conventional dilute acid, dilute alkaline, neutral hot water, steam explosion, and ionic liquid are out of consideration due to the vast wastewater generation, high energy consumption, or high recovery cost of the pretreatment catalyst.[20−23] Ammonia fiber explosion (AFEX) pretreatment meets the criteria[24,25] but is still not completely free of microbial contamination and requires high electricity input for ammonia liquefaction.[25,26] On the other hand, a modified dilute acid pretreatment, dry acid pretreatment, demonstrated the favorable properties for operating at regional collection depots by its zero wastewater generation, low equipment erosion, and solid particle product with a low pH environment.[27−30] The dry acid-pretreated feedstock contains a moderate moisture (~50%, w/w), which is low enough to keep the pretreated feedstock in the solid particle form, but is high enough to keep away from flammability. A previous modeling case study shows that the dry acid pretreatment at regional collection depots leads to the increased collection radius of the feedstock for the construction of extra-large biorefinery plants.[31]

Here, we investigated and verified the year-round storage of three major agricultural crop residues, corn stover, wheat straw, and rice straw under the scenario of performing dry acid pretreatment at the regional collection depots in their major planting regions of China. During year-round storage at different regions, the pretreated feedstocks were periodically evaluated in terms of their physical properties, compositions, enzymatic hydrolysis property, and ethanol fermentability. A case study was followed on the reduced feedstock transportation cost during the year-round storage. This study provided an efficient and practical logistic system for the large-scale biorefinery plant for biofuel production.

■ MATERIALS AND METHODS

Crop Residue Feedstock. Three agricultural crop residue feedstocks used were corn stover, harvested in fall 2017, from Nanyang city, Henan Province, China; wheat straw, harvested in fall 2017, from Jining city, Shandong Province, China; and rice straw, harvested in fall 2017, from Suqian city, Jiangsu Province, China. The virgin feedstocks were coarsely chopped without the de-ashing step (thus with the high ash content of 7.4−10.5%), and finally milled to pass through the mesh with 10 mm in diameter. The compositions of virgin feedstocks were measured according to the NREL protocols with minor modifications based on dry weight base (w/w) and shown in Table S1.[32,33] The detailed procedures of feedstock composition determination are shown in the Supporting Information.

Year-Round Storage Operation of Pretreated Feedstocks. The virgin crop residue feedstocks were dry acid-pretreated and then packed into the disposable polyethylene plastic bags (50 cm × 60 cm in size and 25 μm in thickness). As shown in Figure S1a, every 2 kg of the pretreated feedstock was packed into one bag and coarsely handsealed. The plastic bag was not firmly and strictly airtight. Then, the plastic bags loaded with feedstocks were sent to the selected locations by the Chinese SF Express System within 1 or 2 days' delivery time depending on the locations. For each crop residue feedstock, eight bags (totally 16 kg) were sent to one location. When arrived at the destinations, the feedstocks were placed in the balconies of the buildings at the selected locations (Figure S1b). The outdoor environment included the local temperature, humidity, wind, and partial sunshine, but the rain and snow were kept away.

The year-round storage started on April 1, 2018 and ended on March 31, 2019. During this period, every two bags of the feedstocks (4 kg) were sent back every 3 months by the same SF Express System for the evaluation of the physical properties, hydrolysis yield, and ethanol fermentability. Totally five sets of evaluations were conducted on the freshly pretreated (0 month-stored), and the 3-, 6-, 9-, and 12-month-stored feedstocks, respectively. The specific time points of the evaluation were on July 1, 2018; October 1, 2018; January 1, 2019; and March 31, 2019.

The geographical locations of the storage were selected according to the crop planting quantity and crop residue output. The corn stover was stored along the "Corn Belt of China" regions including (i) Jilin Province with the specific storage location in Jilin University, Changchun city, the provincial capital of Jilin at the geographical coordinates of 43°49′34″N, 125°17′11″E; (ii) Shandong Province with the specific storage location in Qilu University of Technology, Jinan city, the provincial capital of Shandong at 36°33′10″N, 116°48′41″E; and (iii) Henan Province with the specific storage location in Henan Agricultural University, Zhengzhou city, the provincial capital of Henan at 34°47′3″N, 113°39′56″E.

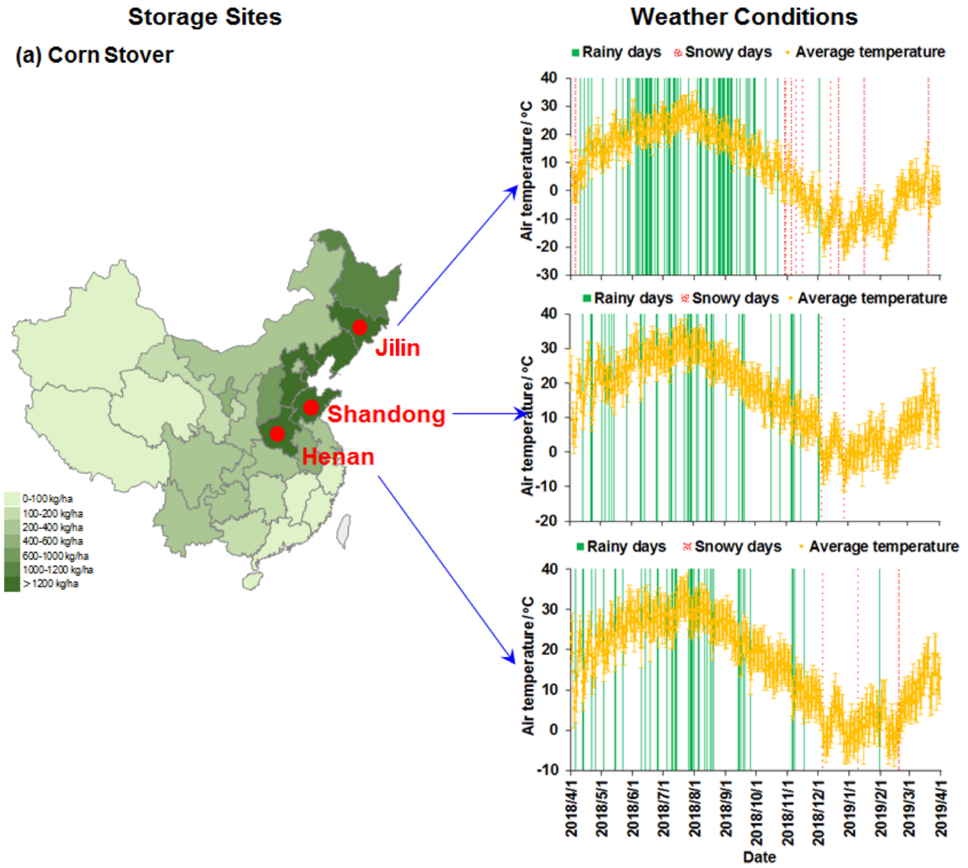
Wheat straw was stored in the wheat planting regions along the Yellow River including (i) Shaanxi Province with the specific storage location in Xi'an Jiao Tong University, Xi'an city, the provincial capital of Shaanxi at 34°14′48″N, 108°59′1″E; (ii) Henan Province with the same storage location as the corn stover in Henan Agricultural University; and (iii) Shandong Province with the same storage location as the corn stover in Qilu University of Technology.

Rice straw was stored along the rice planting regions along the Yangtze River, including (i) Sichuan Province with the specific storage location in Sichuan University, Chengdu city, the provincial capital of Sichuan at 30°33′32″N, 104°0′0″E; (ii) Hubei Province with the specific storage location in Hubei University, Wuhan city, the provincial capital of Hubei at 30°34′43″N, 114°20′1″E; and (iii) Shanghai city (adjacent to Jiangsu Province) with the storage location in East China University of Science and Technology at 31°8′40″N, 121°25′37″E.

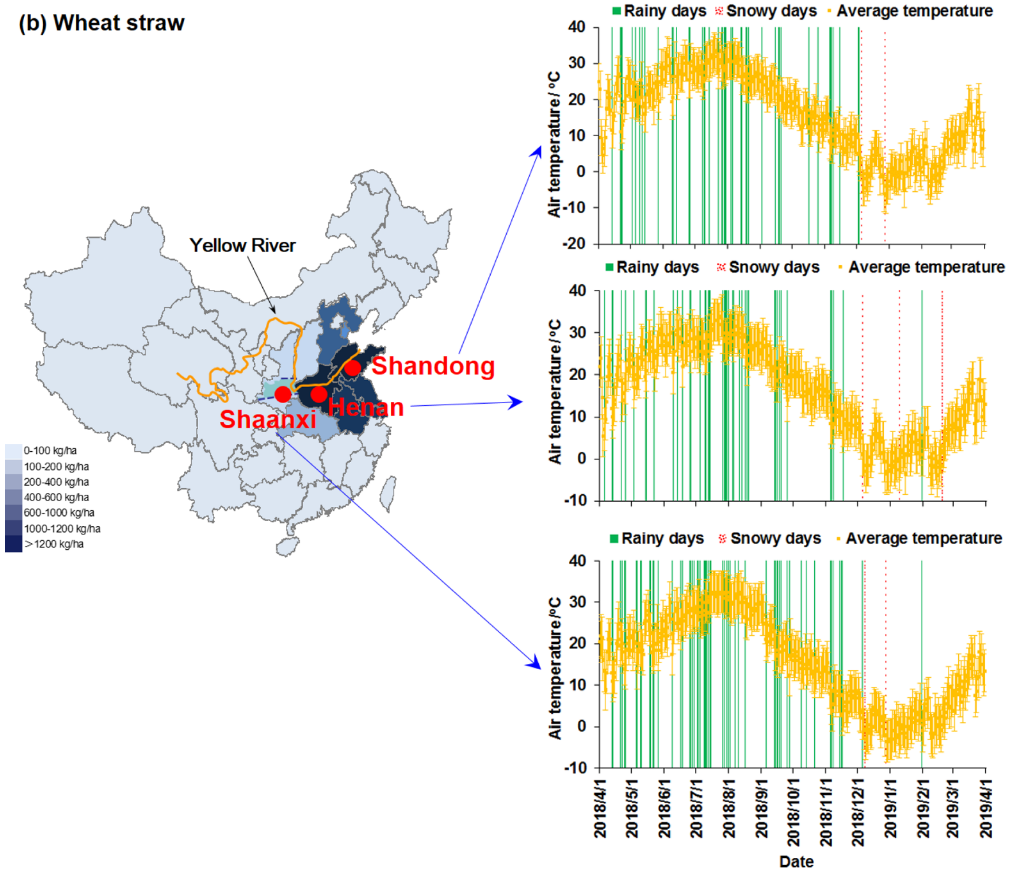
Physical Property Measurement and Calculation. Approximately 30 g of the feedstocks were spread out on a Petri dish plate and photographed. The morphological observation was to observe the potential microbial contaminations during the storage.

The moisture content was determined according to Sluiter et al. by drying the biomass samples to a constant weight at 105 °C.[32]

The bulk and tapped densities were measured according to Hoover et al. using a 437 mL stainless-steel cuboid container with a lid.[34] The biomass sample weight in the full-filled container was recorded and the bulk density was calculated. For tapped density measurement, the container filling with the biomass samples was freely dropped from 15 cm high to the ground and repeated 25 times, then the volume of the tapped samples was measured and the tapped density was calculated. All measurements were repeated twice.



(a) Corn Stover



(b) Wheat straw

Figure 1. continued

https://dx.doi.org/10.1021/acssuschemeng.0c08739
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

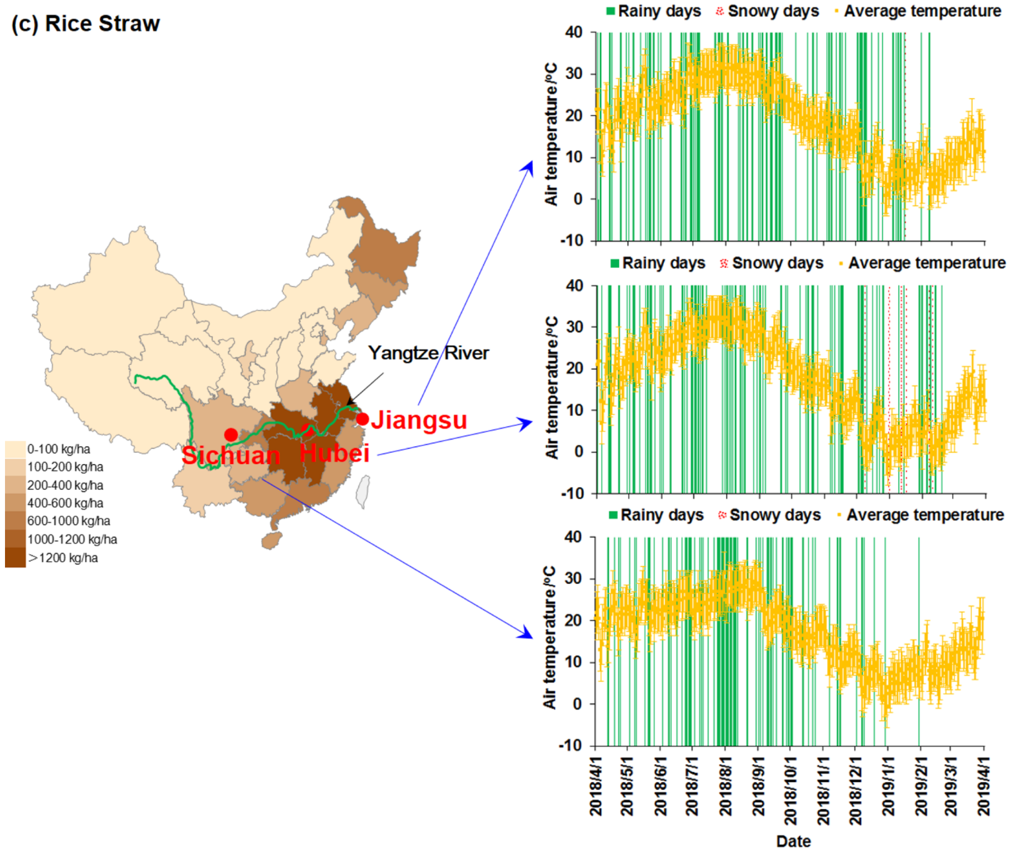


Figure 1. Distribution density of corn stover (a), wheat straw (b), and rice straw (c) in mainland China (excluding Hong Kong, Marco, and South China Sea islands) and the local climate information during year-round storage. Notes: (I) the distribution density of wheat straw in Shaanxi Province was calculated based on the area of the central Shaanxi with the major wheat production, instead of the total provincial area; (II) the distribution density of rice straw in Sichuan was relatively low, but the agriculture land area is large and the overall production was representative; (III) the storage regions were represented by their capital cities (Changchun city for Jilin Province, Jinan city for Shandong Province, Zhengzhou city for Henan Province, Xi'an city for Shaanxi Province, Chengdu city for Sichuan Province, Wuhan city for Hubei Province, except that Jiangsu Province was represented by the adjacent city Shanghai); and (IV) the weather conditions of the storage sites (red dots) represented by the corresponding provincial cities during the year-round storage were shown. Green vertical lines, rainy days; red vertical dotted lines, snow days; yellow vertical lines, range of temperature change within 1 day; (V) yellow line in panel b, Yellow River, which is the major wheat planting region in China; green line in panel c, Yangtze River, which is the major rice planting region in China.

Calculation of the Crop Residue Distribution Density. The distribution density ρ of a specific crop residue (corn stover, wheat straw, or rice straw) is defined as the kilogram per hectare (kg/ha) in a given provincial area of China and is calculated using eq 1

$$\rho = M/S = (G \times R)/S \qquad (1)$$

where M is the total annual output of the specific crop residue in a defined region (kg), S is the total area of this region (hectare), G is the annual output of the crop grain (corn, wheat, or rice) in this region (kg), and R is the ratio of the crop residue weight to the crop grain weight. In this study, the R values were cited from Qiu et al. which are 1.25 for corn stover, 0.95 for wheat straw, and 1.30 for rice straw, respectively.[35]

Transportation Cost Estimation. The central biorefinery is specified as a super-large plant with the annual processing capacity of 10 million metric tons of crop residue feedstock (30,000 metric tons per day), equivalent to the average capability of the petroleum refining plant.[31] The transportation cost of the feedstocks from the collection depots to the central biorefinery plant is calculated without considering the collection operation cost inside the depot according to eq 2[3,31]

$$C = \frac{\sum_{i=1}^{n} Q_i \beta L_i P}{\sum_{i=1}^{n} Q_i} \cdot \frac{1}{Y} \qquad (2)$$

where C is the overall transportation cost of the pretreated feedstocks from the collection depots to the central plant per gallon of fuel ethanol (\$/gal) and n is the collection depot number; the processing capacity of one depot is 300 metric ton per day. The number of depots was cited from Liu and Bao.[31] P is the kilometer transportation cost per ton of the feedstock (\$/(metric ton·km)); $P = P_v/[\rho(1 - w)]$, in which P_v is the kilometer transportation cost per cubic meter of cargo (\$/(m^3·km)) (the average value of 0.07 was used for the regions in this study),[36] ρ is the tapped density of the pretreated feedstocks (metric ton/m^3), w is the moisture content of tapped feedstocks (%); Q_i is the available quantity of the feedstocks in the ith collection area (metric ton); β is the road tortuosity factor with an average value of 1.5 for the regions in this study;[36] L_i is the theoretical straight transport distance of feedstocks from the ith collection depot to the biorefinery plant (km);[3] and Y is the ethanol yield of the feedstock (gal/metric ton) according to the results in this study (76.73, 83.95, and 75.25 for corn stover, wheat straw, and rice straw, respectively). The transportation cost was based on the year of 2017 as reference. The exchange rate from US dollar (\$) to Chinese Yuan (CNY) is 1:6.2.

Enzymes and Reagents. The commercial cellulase Cellic CTec 2.0 was purchased from Novozymes (Beijing, China). The filter paper activity was 203.2 FPU/mL, as determined by the NERL protocol LAP-006;[37] the cellobiase activity was found to be 4900 CBU/mL according to the method described by Ghose;[38] and the protein content was 87.3 mg/mL, as determined by the Bradford method.[39]

Analytically pure glucose, KH_2PO_4, $MgSO_4$, $(NH_4)_2SO_4$, $Ca(OH)_2$, and sulfuric acid (98%, w/w) were purchased from Shanghai Lingfeng Chemical Reagent, Shanghai, China. The yeast extract was from Oxoid, Hampshire, UK.

Dry Acid Pretreatment. Corn stover, wheat straw, and rice straw were pretreated using the dry acid pretreatment procedure with sulfuric acid as the catalyst according to our previous publications.[27,28] The sulfuric acid dosage was adjusted using the base pH approaching method to eliminate the influence of ash in crop residues on pretreatment efficiency.[40] The determined sulfuric acid dosage was 36, 40, and 43 mg sulfuric acid/g corn stover, wheat straw, and rice straw, respectively, on dry weight base. Before the injection of hot steam, the total weight of one batch pretreatment was 1800 g at the dry solid/liquid of 2:1 (w/w), equivalent to ~0.04 kg of the sulfuric acid catalyst, and ~0.5 kg of water per kg of the crop residue feedstock. The feedstock and catalyst were concurrently fed into the 20 L pretreatment reactor equipped with a single helical ribbon impeller. The saturated water steam (1.6 MPa, 201 °C) was then injected into the reactor, and maintain at 175 °C for 5 min under the mild agitation of 50 rpm. The pretreated feedstocks were gravitationally discharged from the bottom outlet port but no free wastewater was generated due to which the acid solution and condensed water were completely adsorbed into the solid feedstocks. The water content (w/w) in the pretreated corn stover, wheat straw, and rice straw was 56.2, 54.2, and 61.2%, respectively.

Biodetoxification. *Amorphotheca resinae* ZN1 (the storage code is #7452 in China General Microbiological Culture Collection Center, CGMCC, www.cgmcc.net/) was used for the biological removal of inhibitory compounds in the pretreated crop residues.[41,42] *A. resinae* ZN1 was preserved at 4 °C on a potato dextrose agar (PDA) slant before inoculation to pretreated crop residue feedstocks. The spores of *A. resinae* ZN1 were collected from the PDA slant and diluted to approximately $5-6 \times 10^6$ spores per milliliter. The pretreated feedstocks were neutralized with 20% (w/w) calcium hydroxide to pH 5−6, then the spore suspension was inoculated onto the feedstock solids at a weight ratio of 10% (w/w) and cultured for 3 days. The solid-state biodetoxification was carried in a 15 L bioreactor at 28 °C and aeration of 1 vvm (air volume/broth volume/min) until the furfural is completely removed.[42]

Enzymatic Hydrolysis and Ethanol Fermentation. Enzymatic hydrolysis was carried out according to the protocol of NREL LAP-009.[43]

Saccharomyces cerevisiae XH7 was used as the ethanol fermentation strain.[44,45] The first seed culture was prepared in the yeast extract peptone dextrose medium containing 20 g/L glucose, 20 g/L peptone and 10 g/L yeast extract at 30 °C and 200 rpm for 12 h. The second seed culture was prepared in the hydrolysate containing 5% (w/w) pretreated and biodetoxified feedstock, 2 g/L KH_2PO_4, 2 g/L $MgSO_4$, 2 g/L $NH_4(SO_4)_2$,10 g/L yeast extract, and 10 mg cellulase protein per gram of cellulose at 10% (v/v) inoculation for 12 h. The third seed culture was the same as the second seed culture, but the solid content increased to 10% (w/w) for 24 h. For simultaneous saccharification and ethanol co-fermentation (SSCF), the pre-hydrolysate was first obtained in a 5 L helical ribbon stirrer-agitated bioreactor at 30% (w/w) solid content, 50 °C, pH 4.8 for 12 h with adding 10 FPU/g DM cellulase, then reduced to 30 °C supplemented with 2 g/L KH_2PO_4, 2 g/L $MgSO_4$, 2 g/L $NH_4(SO_4)_2$, and 10 g/L yeast extract as nutrients. The third seed broth was transferred to pre-hydrolysate, and the fermentation conditions were at 200 rpm for 96 h.

The practical ethanol yield was calculated according to Zhang and Bao.[46] The cell growth in the SSCF process was measured by counting the colony-forming units (CFU), as described by Gu et al.[47]

High-Performance Liquid Chromatography. Glucose, xylose, ethanol, furfural, 5-hydroxymethylfurfural (HMF), and acetic acid in the liquid phase were analyzed by a Shimadzu high-performance liquid chromatography (HPLC) system equipped with a Bio-Rad Aminex HPX-87H column and a RID-10A detector. Sample (20 μL) was subjected and analyzed at 60 °C using 5 mM H_2SO_4 as the eluent with a flow rate of 0.6 mL/min.

RESULTS AND DISCUSSION

Geographical Locations for Year-Round Storage of Three Agricultural Crop Residues. The three major crop residue feedstocks, corn stover, wheat straw, and rice straw, accounting for nearly 80% of the total crop residues in China,[48] were selected for year-round storage after dry acid pretreatment. The geographical locations for year-round storage were selected based on the distribution density of the three crop residues in the major agricultural provinces of China. The annual provincial grain production and the land area data were cited from the National Bureau of Statistics of China (http://www.stats.gov.cn) (Figure 1). The storage regions include (i) the "Corn Belt of China" regions from the northeast, to the east, then to the central China for corn stover (Figure 1a); (ii) the wheat planting regions along the Yellow River region from the northwest, to the central, then to the east regions for wheat straw (Figure 1b); and (iii) the rice planting regions along the Yangtze River from the southwest, to the central, and then to the east regions for rice straw (Figure 1c).

The crop residue feedstock samples were stored in the provincial capital cities to represent the whole high-producing provinces. In detail, corn stover was stored in the Chinese Corn Belt region from the Northeast China region (Jilin Province, represented by Changchun city), to the East China region (Shandong Province, represented by Jinan city), and then to the Central China region (Henan Province, represented by Zhengzhou city) (Figure 1a). Wheat straw was stored in the major wheat planting regions along the Yellow River from the Northwest region (Shaanxi Province, represented by Xi'an city), to the Central region (Henan Province, represented by Zhengzhou city), and to the East region (Shandong Province, represented by Jinan city) (Figure 1b). Rice straw was stored in the major rice planting regions along the Yangtze River from the Southwest region (Sichuan Province, represented by Chengdu city), to the Central region (Hubei Province, represented by Wuhan city), and to the East region (Jiangsu Province, represented by adjacent Shanghai city) (Figure 1c).

The weather records of the storage sites represented by the corresponding provincial cities during the whole storage period (from April 1, 2018 to March 31, 2019) are cited from the China Meteorological Administration (http://www.cma.gov.cn), as illustrated in Figure 1. The data show that the south regions generally were rainy, humid, and hot; the north regions were dry, cold, and less rainy but more snows; and the central regions were in between. The situation indicates that the southern regions face the greater challenge in the long-term storage of feedstocks than the northern regions and the central regions.

Evaluation of Physical, Chemical, and Biological Properties of the Pretreated Feedstocks during Year-Round Storage. The morphology of the freshly pretreated and of the year-round stored feedstocks is shown in Figure 2. The pretreated feedstock is in the solid particle form. No observable morphology differences were found for all the crop residue samples after year-round storage at different storage locations. Meanwhile, no visual microbial contaminations in the year-round stored feedstocks were observed. The constant content of the total fermentable sugars (cellulose, glu-oligo, glucose, xylan, xylo-oligos, and xylose) in the pretreated feedstocks during the storage (Table S2) further indicated that

Figure 2. Morphological observation of the freshly pretreated and year-round stored crop residue feedstocks in different regions.

there was no microbial contamination on dry acid-pretreated feedstocks during the storage.

The physical property evaluation of the dry acid-pretreated crop residue feedstocks compared to virgin feedstock is shown in Table S3. The feedstocks absorbed the hot steam and acid solution during the pretreatment, the moisture content of pretreated feedstocks reached over 50% (w/w). Meanwhile, the bulk density and tapped density of feedstocks are significantly higher than those of the virgin feedstock, indicating that dry acid pretreatment can densify the feedstocks. The periodical physical property changes in the crop residue feedstocks during the year-round storage period are shown in Figure 3. The moisture content, bulk density, and tapped density of all the feedstocks at different locations were generally maintained constant. The moisture content was slightly reduced due to the slow evaporation from the loosely sealed plastic bags (Figure 3a). The reduced moisture content also led to the slow increase of the bulk and tapped densities (Figure 3b,c), which was positive for reducing the transportation cost from collection depots to the central biorefinery plant. It is worth noting that the decrease in the moisture content during the long-term storage is partially related to the evaporation of volatile compounds in addition to water. These volatile compounds, including furfural, HMF, acetic acid, formic acid, and so forth produced from pretreatment, are a part of the pretreated feedstocks, which is about 9−10% of dry matter weight. The evaporation of volatile compounds usually results in an overestimation of the actual moisture content, as estimated by the general method to determine the moisture content,[32] especially in the characterization of feedstocks with a high solid content.

The compositions of virgin feedstocks are shown in Table S1. The compositional changes of the crop residue feedstocks during year-round storage are shown in Table S2 and S4. After dry acid pretreatment, most hemicellulose of feedstocks was hydrolyzed and cellulose remained stable. Various lignocellulose-derived inhibitory compounds, such as furfural, HMF, and acetic acid, were generated due to the harsh conditions of pretreatment (Table S1 and S2). These compounds severely inhibit the consequent fermenting microbes, which need to be effectively removed.[41]

Although, the temperature and humidity are in wide variations at different storage locations (Figure 1), the cellulose content was basically constant with the change of less than 6% during the year-round storage of pretreated feedstocks at different regions, while the xylan content slightly decreased by 14−35% due to the weak hydrolysis of hemicellulose to xylo-oligo or xylose by the residual sulfuric acid catalyst in the pretreated crop residue feedstocks (Table S4). The slow xylan hydrolysis also released acetyl groups into acetic acid generation. The soluble hexose and pentose sugars (glucose, xylose, and their oligosaccharides) were relatively constant. For the inhibitory compounds, acetic acid slightly increased owing to the slow xylan hydrolysis, while furfural decreased by an average of 83, 97, and 79% for corn stover, wheat straw, and rice straw at different storage regions, and HMF decreased by an average of 48, 53, and 68%, respectively, after year-round storage due to the ventilation in the loosely sealed plastic bags (Tables S2 and S4). The evaporation of furfural was 5.2, 7.0, and 2.2 g per ton of the pretreated corn stover, wheat straw, and rice straw (dry base), while HMF was 4.0, 2.9, and 3.8 g per ton of the pretreated feedstocks, respectively. Although the evaporation of the partial inhibitors relieved the subsequent biodetoxification intensity, the release in a narrow feedstock packing space could generate the off-gases containing high contents of furfural and HMF, which may be potentially toxic to humans. Therefore, ventilation and/or absorption systems should be considered at the depots packing lots. The total matter loss of three dry acid-pretreated crop residue feedstocks is less than 7% after year-round storage at different storage regions (Table S4), mainly due to the evaporation of furfural and HMF, rather than the loss of fermentable sugars.

The enzymatic hydrolysis capacity and fermentability evaluation (tested by cellulosic ethanol fermentation) of the crop residue feedstocks during year-round storage were conducted periodically (Figure 4). The hydrolysis yield of the feedstocks maintained constant or slightly increased during the year-round storage period, regardless of the feedstock types, storage regions, and time (Figure 4a), due to the slow xylan degradation and slight cellulose decomposition by sulfuric acid inside the feedstocks. The reduction of furfural and HMF may also contribute to the increase of the hydrolysis yield by the relieved inhibition on cellulase activity. Similarly, the periodical ethanol fermentability evaluation was conducted by simultaneous saccharification and co-fermentation (SSCF) under the high feedstock solid loading of 30% (w/w) after biodetoxification (Figure 4b). The ethanol productions using different feedstocks were constant, regardless of the feedstock types, storage regions, or time. The results indicate that year-round storage had no negative impact on the hydrolysis yield and ethanol fermentability of the crop residue feedstocks.

https://dx.doi.org/10.1021/acssuschemeng.0c08739
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

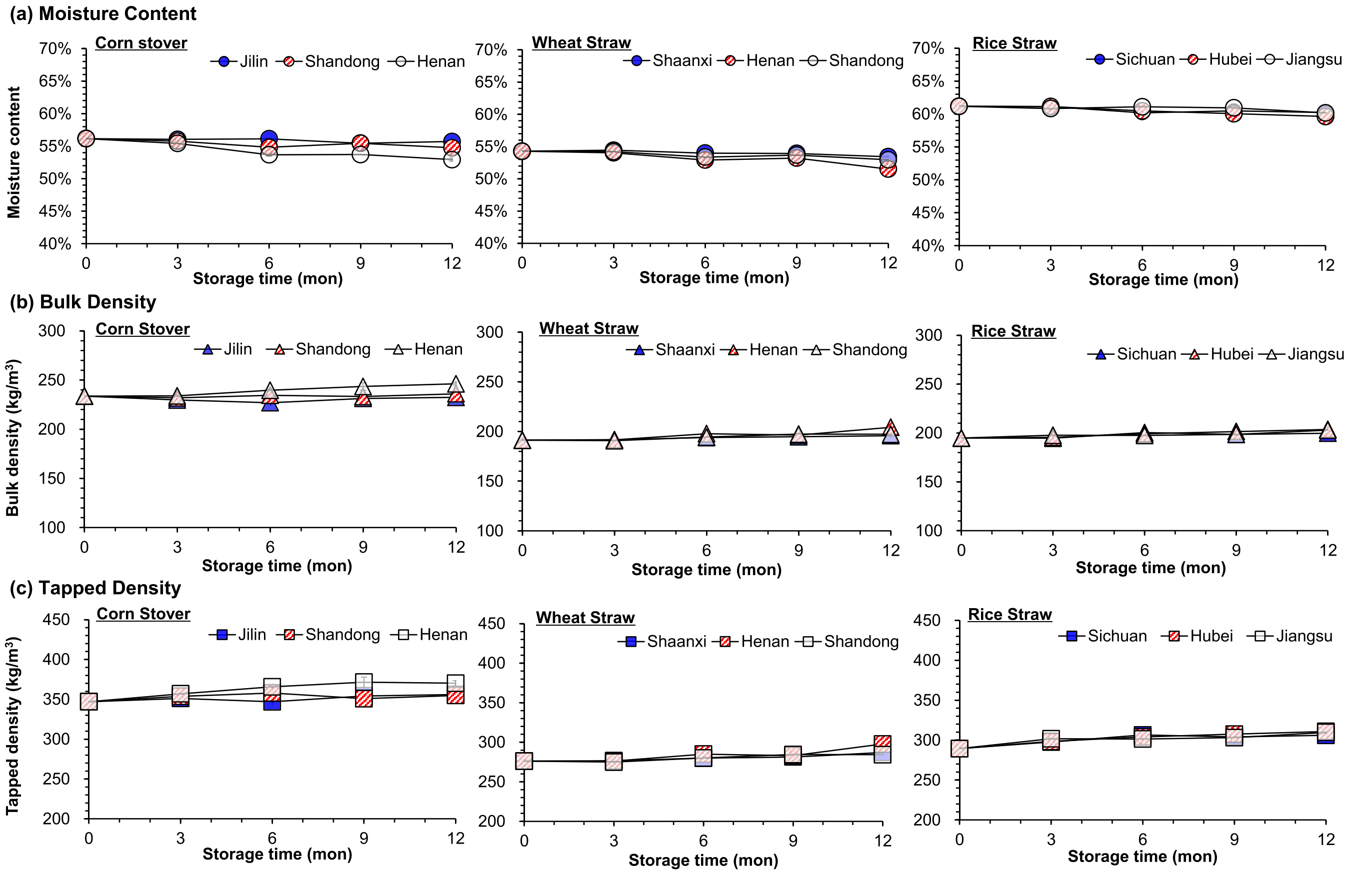


Figure 3. Physical property evaluation of the dry acid-pretreated crop residue feedstocks during year-round storage in different regions. The changes in the moisture content of feedstocks in different cities during 12 months: (a) Changes in the bulk density of feedstocks in different cities during 12 months, (b) changes in the tapped density of feedstocks in different cities during 12 months, and (c) bulk and tapped densities calculated based on the dry weight of pretreated feedstocks. Bulk density (kg/m^3); tapped density (kg/m^3).

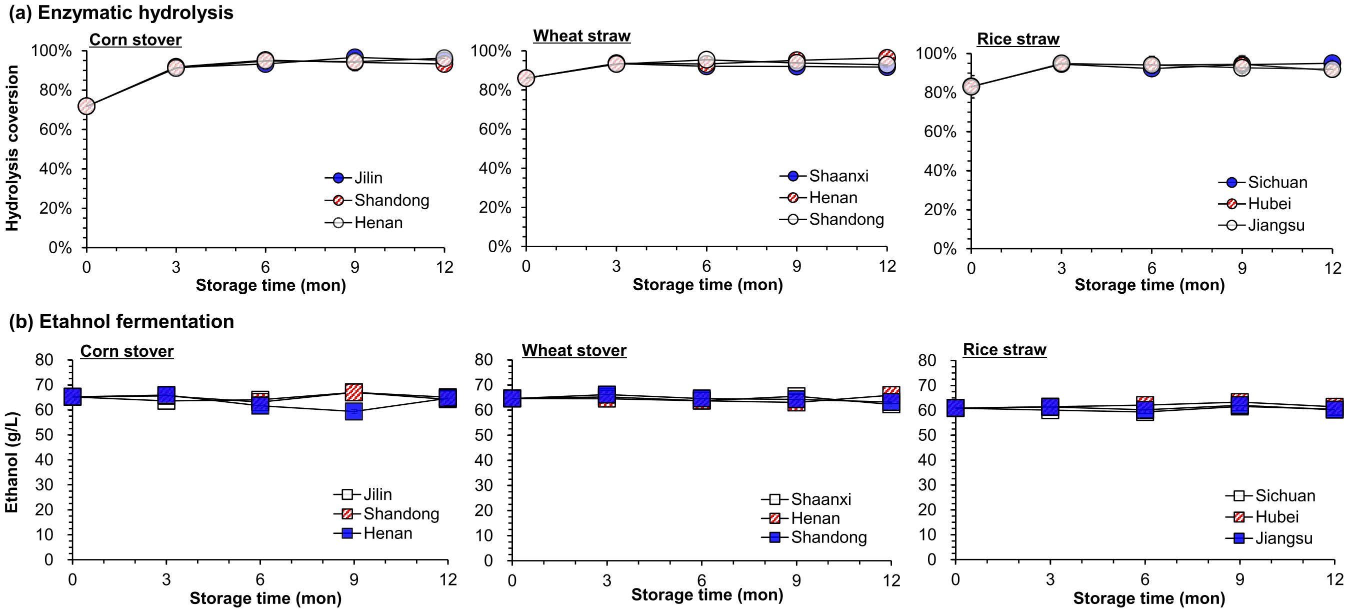
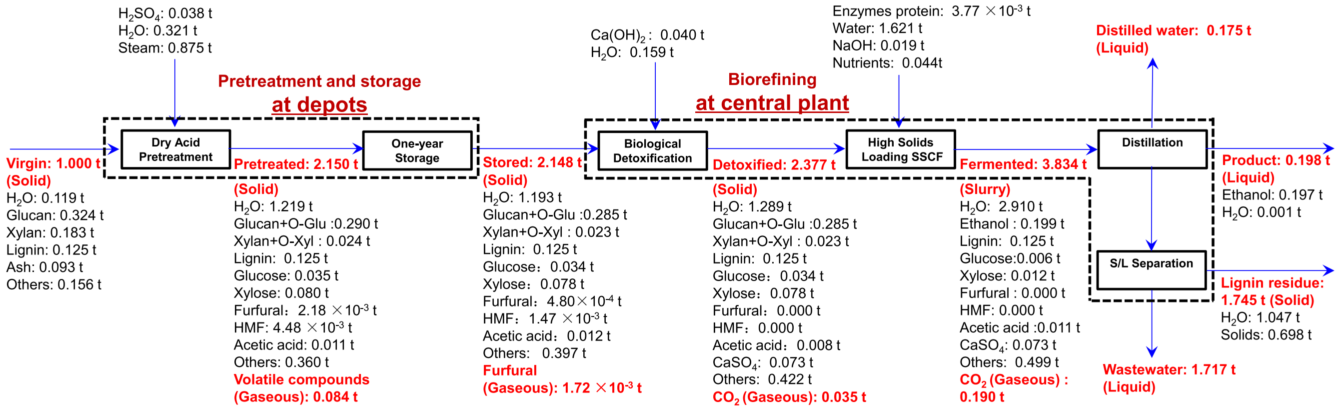


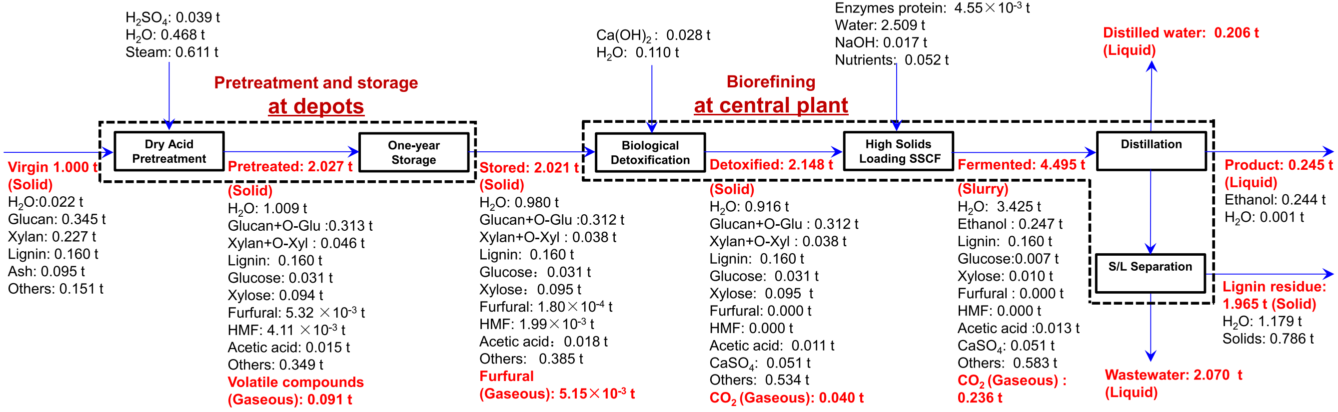
Figure 4. Hydrolysis and fermentability evaluation of the pretreated crop residue feedstocks during the year-round storage in different regions. (a) Enzymatic hydrolysis conversion. The enzymatic hydrolysis yield evaluation of pretreated feedstocks was carried out according to the protocol of NREL LAP-009.[43] (b) Fermentability (tested by cellulosic ethanol fermentation) of the pretreated feedstocks. The ethanol fermentability was indicated by the final ethanol concentration after 96 h of SSCF.

Compared with our previous studies,[30] the ethanol production in this study was relatively low (64.7 versus 78.7 g/L for corn stover, 63.8 versus 88.0 g/L for wheat straw, or by ethanol yield of 75.7 versus 84.7% for corn stover, 73.9 versus

(a) Mass balance of corn stover in dry biorefining process



(b) Mass balance of wheat straw in dry biorefining process



(c) Mass balance of rice straw in dry biorefining process

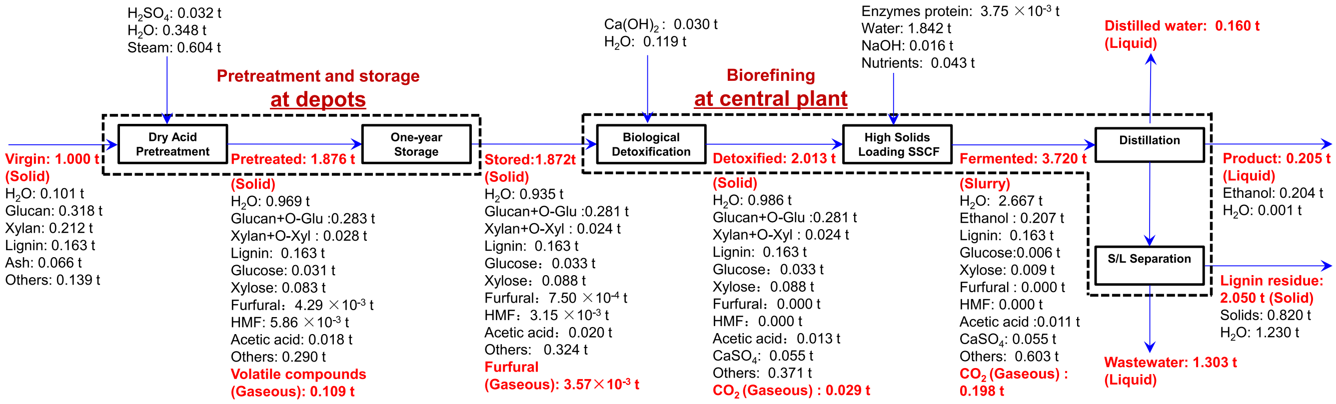


Figure 5. Mass balance of the three crop residue feedstocks in the dry biorefining process.

82.8% for wheat straw). The major reason came from the higher ash content (7.4–10.5%) because no deashing step was conducted in this study for the purpose of achieving the realistic scenario of storage. Under high-solid-loading fermentation, the higher ash content leads to the decrease of fermentable sugar content at the same solid loading (30%, w/w) for SSCF. The almost doubled ash content in the feedstocks (7.4 vs 3.5% for corn stover, 9.7 vs 5.2% for wheat straw) in this study not only led to the low cellulose content in the pretreated feedstocks (29.2 vs 33.6% for corn stover; 28.6 vs 36.9% for wheat straw)[25] but also significantly affected the fermentation efficiency.

Mass Balance in the Biorefining Chain and Transportation Cost Calculation in Year-Round Storage. The dry biorefining chain and the mass balance (take cellulosic ethanol production, for example) of one metric ton of corn stover (a), wheat straw (b), or rice straw (c) to ethanol is briefly illustrated in Figure 5 based on the experimental results (Tables S1–S2, Figures 3 and 4). The dry biorefining chain includes dry acid pretreatment and year-round storage carried out at local depots, biodetoxification, saccharification and fermentation, distillation, and solid/liquid separation carried out at the central biorefinery plant. For one metric ton of virgin corn stover (including 10.1% of water and 7.4% of ash), the pretreatment step produced 1.876 tons of pretreated feedstock, and 0.109 tons of volatile compounds from excessive degradation of corn stover with absorbing 0.604 ton of steam and 0.38 ton of sulfuric acid solution. The year-round storage led to the free release of 82.5% furfural and 46.2% HMF and slight increase of acetic acid, but the total fermentable sugars (cellulose/xylan, glu-/xyl-oligomers, glucose/xylose) were relatively constant. The biodetoxification step completely removed furfural and HMF, partially acetic acid (~35.0%), while the sugars were almost constant without any observable loss after the corn stover was transported to the central plant. The sulfuric acid catalyst in the pretreated corn stover was neutralized by calcium hydroxide and generated 0.055 ton of calcium sulfate solids. The enzymatic hydrolysis (saccharification) and fermentation steps produced 0.207 tons of ethanol and 0.198 tons of CO_2 with the residual sugars (5.94×10^{-3} ton of glucose and 9.43×10^{-3} ton of xylose). The distillation and solid/liquid separation steps produced 0.205 tons of ethanol product (99.5%, v/v), 2.050 tons of lignin residue (including 1.230 tons of H_2O, and 0.820 tons of solids composed of lignin, calcium sulfate, and other substance), and 1.303 tons of wastewater (Figure 5a). The distilled water (0.160 tons) generated in ethanol recovery process can be recycled directly.

Similar mass balances occur for wheat straw and rice straw: one metric ton of raw wheat straw (2.2% of water and 9.5% of ash) finally produced 0.244 tons of ethanol product, 1.965 tons of lignin residue (including 1.179 tons of H_2O and 0.789 tons of solids), and 2.070 tons of wastewater (Figure 5b); one metric ton of raw rice straw (with water content of 11.9% and ash content of 9.3%) finally produced 0.198 tons of ethanol product, 1.745 tons of lignin residue (including 1.047 tons of H_2O and 0.698 tons of solids), and 1.717 tons of wastewater (Figure 5c). The overall ethanol yield from the dry corn stover, wheat straw, or rice straw was 75.7, 83.8, and 76.4% of the theoretical values, respectively. The results are based on the experimental results of year-round storage using the crop residue feedstocks without the de-ashing operation, therefore, the ethanol yield and titer were lower than those while using the de-ashed feedstocks, which is a conventional operation.[28,30]

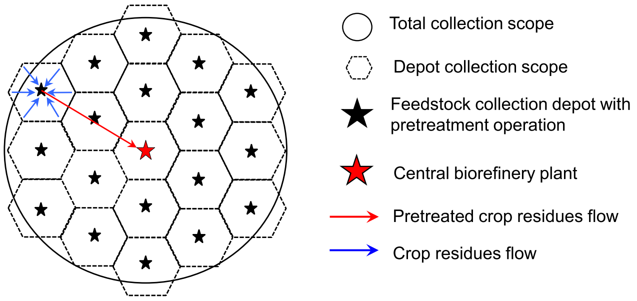
The feedstock transportation cost accounts for 35−50% of the overall production cost of cellulosic ethanol.[49] The present year-round storage result supports a feasible low-cost transportation strategy because of the high and constant feedstock density after dry-acid pretreatment. The tapped densities (ton/m^3) of virgin feedstocks, raw pretreated feedstocks, and year-round stored pretreated feedstocks are shown in Table 1. After year-round storage, the tapped densities of the feedstocks were slightly increased compared to those of freshly pretreated feedstocks, owing to the reduction of the moisture content.

Table 1. Tapped Densities (ton/m^3) of the Feedstocks before and after Pretreatment and Storage[a]

biomass type	storage regions	virgin feedstock	freshly pretreated	after 1 year
corn stover	Jilin	0.115	0.347	0.356
	Shandong	0.115	0.347	0.355
	Henan	0.115	0.347	0.370
wheat straw	Shandong	0.116	0.276	0.284
	Shaanxi	0.116	0.276	0.287
	Henan	0.116	0.276	0.298
rice straw	Sichuan	0.058	0.289	0.306
	Jiangsu	0.058	0.289	0.310
	Hubei	0.058	0.289	0.311

[a] Virgin feedstock refers to the raw crop residues after harvest and air-drying and then crushed to 40−60 mesh; freshly pretreated refers to the pretreated feedstocks without long-term storage; after 1 year refers to the pretreated feedstocks with year-round storage.

The transportation cost calculation is based on the supply of the super large biorefinery plant with the annual feedstock processing capacity of 10 million metric tons (30,000 tons per day), equivalent to the average capability of the petroleum refining plant.[31] The feedstock is harvested and pretreated in various collection depots, as shown in Figure 6. Only the transportation cost from the depots to the central plant is taken into account. The raw crop residues are collected, dried and crushed by local depots, and then sent to be dry acid-pretreated on site. The pretreated feedstocks are then directly stored in local depots and periodically transported to the central biorefinery plant for biodetoxification and bioethanol production.



Regions	Collectable density[a] (ton/km^2)	Collection radius[b] (km)	Depot number[c]
Jilin	109.38	170.63	99
Shandong	85.30	193.22	127
Henan	138.09	151.87	78
Shaanxi	9.56	577.10	1142
Sichuan	19.77	401.35	552
Jiangsu	177.18	134.07	60
Hubei	68.28	215.97	159

Figure 6. Transportation cost model of the dry acid-pretreated feedstocks to the central biorefinery plant. This model is used to calculate the transportation cost ($/gal ethanol) of the pretreated crop residue from each depot to the central biorefining plant (straight red line distance). The collection cost and the transportation cost inside the depots before pretreatment were not taken into account (straight blue line distance). [a]Crop residue distribution density (ton/km^2) in each stored province (sum of wheat straw, corn stover and rice straw). [b]Collection radius (km) of the total collection scope, the collection radius can meet the demand of the central biorefinery with a processing capacity of annual 10 million metric tons (30,000 metric tons daily) in the corresponding stored province. [c]Depot number, the number of depots in one collection scope meeting the demand of the central biorefinery with a processing capacity of annual 10 million metric tons. The processing capacity of one depot is 300 metric ton per day. The number of depots was cited from Liu and Bao.[31] The collection radius and the depot number for one collection region are calculated based on the full operation of the central plant (10 million metric tons of feedstocks annually), as well as the distribution density of the crop residues in the storage regions.

Table 2 shows the transportation costs ($/gal ethanol) of the virgin feedstock, the freshly pretreated feedstock and the periodically stored (3, 6, 9, or 12 months) feedstock from the depots to the central plant. A region generally has one or two dominant crop residues, thus the transportation cost of one specific crop residue is calculated in a certain period, while the rest of the period is another feedstock. The transportation costs of the freshly pretreated corn stover, wheat straw, and rice straw from the depots to the central plant are reduced by 67, 58, and 80%, compared with that of the virgin feedstocks

Table 2. Transportation Costs ($/gal Ethanol) of the Feedstock from Collection Depots to the Central Biorefinery Plant by the Decentralized Storage Method

	storage regions	virgin feedstock	freshly pretreated	after 3 months	after 6 months	after 9 months	after 1 year	transportation period ratio[a] (%)
corn stover	Jilin	1.36	0.45	0.45	0.45	0.44	0.44	82
	Shandong	1.54	0.51	0.50	0.50	0.50	0.50	52
	Henan	1.11	0.37	0.32	0.35	0.34	0.34	38
wheat straw	Shandong	1.35	0.57	0.57	0.56	0.55	0.55	45
	Shaanxi	3.28	1.38	1.38	1.36	1.35	1.33	30
	Henan	1.01	0.43	0.43	0.41	0.42	0.40	52
rice straw	Sichuan	6.42	1.29	1.25	1.22	1.23	1.22	60
	Jiangsu	3.08	0.62	0.59	0.59	0.59	0.58	65
	Hubei	3.97	0.80	0.77	0.76	0.75	0.74	75

[a] The transportation ratio of this species crop residue in the total crop residue transportation period throughout the year. The collection, transportation, and supply of a single crop residue (such as corn stover) are limited by its annual output, in order to meet the normal operation of the central cellulose ethanol biorefinery plant with an annual processing capacity of 10 million metric tons of feedstocks, it will be supplemented with other crop residues (such as wheat straw and rice straw, assuming that their basic properties are similar to corn stover) when a single crop residue is not enough to supply.

(without dry acid pretreatment). During year-round storage at the collection depots, the transportation cost continues to decrease slowly due to the gradual increase of the feedstock density (Figure 3c). For wheat straw in the Henan province, rice straw in the Jiangsu province, and wheat straw in the Hubei province, the transportation cost of year-round stored feedstocks decreased by 7.3, 6.5, and 6.9%, respectively, compared with the freshly pretreated feedstocks. The minimum transportation cost is for corn stover in the Henan Province due to the high collectable density (0.34 $/gal ethanol). The results suggest that the increase of the feedstock density by dry acid pretreatment and year-round storage significantly reduced the cost of the off-depot transportation, compared with the traditional mode of virgin feedstock collection, transportation, and processing.

The long-term storage of virgin feedstocks (without pretreatment) had been conducted and discussed in the previous publications. Brand et al. reported that the optimal storage time of different virgin feedstocks only ranged from 2–4 months, before it was decayed apparently.[50] Nurmi argues that, even with drying occurring in the summer, moisture is nonetheless reabsorbed if storage is extended over the autumn or winter months,[51] and the high moisture content directly results in fungal growth and mass loss. On the other hand, the low density of virgin feedstock, even after mechanical densification, still leads to highly expensive transportation cost. The dry acid pretreatment method provides a practical basis for the storage operation by its ability for high preservation of polysaccharide solids, highly compacted accumulation density, being free from wastewater generation, low capital investment, and low energy consumption. Three major agricultural crop residues, corn stover, wheat straw, and corn stover were pretreated using the dry acid pretreatment method and then stored in their major planting regions under varying natural conditions of temperature, rain and snow falling, humidity, wind, and sunlight. During the year-round storage, no obvious sugar loss was observed; the bulk and taped densities kept constant or even slightly increased; the enzymatic hydrolysis yield and fermentability (tested by cellulosic ethanol fermentation) were stable and with slight increase. The above-presented case study shows that the feedstock transportation cost of the long-term stored feedstocks under the scenario of dry acid pretreatment at collection depots was significantly reduced compared to that of the direct transportation of virgin crop residual feedstocks. This study provided an efficient and practical logistic system for a large-scale biorefinery plant.

■ CONCLUSIONS

A new method of year-round storage of three major agricultural crop residues, corn stover, wheat straw, and rice straw, was proposed and experimentally verified under the scenario of performing dry acid pretreatment at the distributed regional collection depots. The dry acid pretreatment method lays the foundation of the year-round storage operation at the depots by its ability for high preservation of polysaccharide solids, highly compacted accumulation density, being free from wastewater generation, low capital investment, and low energy consumption. The pretreated agricultural crop residues were stored in their major planting regions varying largely in natural conditions such as temperature, rain and snow fall, humidity, wind, and sunlight. The results show that the pretreated feedstocks after year-round storage in different regions were well preserved with negligible solid and fermentable sugar loss and highly compacted density. The physical properties, compositions, enzymatic hydrolysis yield property, and ethanol fermentability of the feedstocks were approximately constant after year-round storage, with a few positive exceptions such as the increased hydrolysis yield and lessened inhibitor content. A case study shows that the feedstock transportation cost of stored pretreated feedstocks from the collection depots to the central biorefinery plant was significantly reduced compared to that of the virgin crop residue feedstocks. This study provided an important method and a strategy for the long-term storage of lignocellulose feedstocks to the logistic system of the large-scale biorefinery plant for the production of cellulosic biobased products.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c08739.

Compositions (% DM) of virgin crop residue feedstocks; detailed procedures of feedstock composition determination; photos of the packed bag loaded with pretreated feedstock and the outdoor environment of the storage location; compositions of the dry acid-pretreated crop residue feedstocks in different regions during 1 year storage; physical property evaluation of the dry acid-pretreated crop residue feedstocks as compared to virgin feedstocks; and compositional matter change (%) after 1 year storage as compared to freshly pretreated feedstocks (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jie Bao − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China;* orcid.org/0000-0001-6521-3099; Phone: +86 21 64251799; Email: jbao@ecust.edu.cn

Authors

Tao Han − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China*

Bin Zhang − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China*

Hongxing Li − *State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, Shandong 250353, China*

Hongsen Zhang − *College of Life Science, Henan Agricultural University, Zhengzhou, Henan 450002, China*

Yongfu Yang − *State Key Laboratory of Biocatalysis and Enzyme Engineering, School of Life Sciences, Hubei University, Wuhan, Hubei 430062, China*

Lizhen Hu − *School of Chemical Engineering and Technology, Xi'an Jiao Tong University, Xi'an, Shaanxi 710049, China*

Xiaodong Ren − *School of Life Science, Jilin University, Changchun, Jilin 130012, China*

Shipeng Wang − *College of Architecture and Environment, Sichuan University, Chengdu, Sichuan 610065, China*

Lixiang Zheng − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China*

Xushen Han − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China*

Gang Liu − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China*

Jian Zhang − *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai 200237, China;* orcid.org/0000-0001-7833-5634

Qiang Fei − *School of Chemical Engineering and Technology, Xi'an Jiao Tong University, Xi'an, Shaanxi 710049, China;* orcid.org/0000-0002-6716-649X

Yueqin Tang − *College of Architecture and Environment, Sichuan University, Chengdu, Sichuan 610065, China;* orcid.org/0000-0001-6872-1099

Shihui Yang − *State Key Laboratory of Biocatalysis and Enzyme Engineering, School of Life Sciences, Hubei University, Wuhan, Hubei 430062, China;* orcid.org/0000-0002-9394-9148

Xiaoming Bao − *State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, Shandong 250353, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c08739

Author Contributions

T.H. and B.Z. equally contributed to this work. T.H., L.Z., X.H., and G.L. collected the feedstocks, organized the transportation, and performed the storage of rice straw in Shanghai; T.H. and B.Z. performed the biorefinery evaluation and analyzed the evaluation. L.Z., G.L., and J.Z. helped the biorefinery evaluation; H.L. and X.B. performed the storage of corn stover and wheat straw in Shandong and provided the fermentation strain; H.Z. performed the storage of corn stover and wheat straw in Henan; Y.Y. and S.Y. performed the storage of rice straw in Hubei; X.R. performed the storage of corn stover in Jilin; S.W. and Y.T. performed the storage of rice straw in Sichuan; L.H. and Q.F. performed the storage of wheat straw in Shaanxi; J.B. conceived and directed the experiment; T.H., B.Z., and J.B. drafted the manuscript. All the authors contributed to analysis and manuscript writing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (31961133006 and 21978083).

■ NOMENCLATURES

ρ, distribution density of the specific crop residue, kg/ha
M, total annual output of the specific crop residue in a defined region, kg
S, total area of this region, hectare
G, annual output of the crop grain in this region, kg
R, ratio of the crop residue weight to the crop grain weight
C, overall transportation cost of the pretreated feedstocks from the collection depots to the central plant per gallon of fuel ethanol, \$/gal
Q_i, available quantity of the feedstocks in the ith collection area, metric ton
β, road tortuosity factor
L_i, theoretical straight transport distance of feedstocks from the ith collection depot to the biorefinery plant, km
P, kilometer transportation cost per ton of the feedstock, \$/(metric ton·km)
P_v, kilometer transportation cost per cubic meter of cargo, \$/(m^3·km)
ρ, tapped density of the pretreated feedstocks, metric ton/m^3
w, moisture content of tapped feedstocks, %
Y, ethanol yield of the feedstock, gal/metric ton

■ REFERENCES

(1) Eranki, P. L.; Bals, B. D.; Dale, B. E. Advanced Regional Biomass Processing Depots: A key to the logistical challenges of the cellulosic biofuel industry. *Biofuels, Bioprod. Biorefin.* **2011**, *5*, 621−630.

(2) Dale, B. A sober view of the difficulties in scaling cellulosic biofuels. *Biofuels, Bioprod. Biorefin.* **2017**, *11*, 5−7.

(3) Kim, S.; Dale, B. E. Comparing alternative cellulosic biomass biorefining systems: Centralized versus distributed processing systems. *Biomass Bioenergy* **2015**, *74*, 135−147.

(4) Womac, A. R.; Igathinathane, C.; Sokhansanj, S.; Pordesimo, L. O. Biomass Moisture Relations of an Agricultural Field Residue: Corn Stover. *Trans. ASAE* **2005**, *48*, 2073−2083.

(5) Han, X.; Hong, F.; Liu, G.; Bao, J. An Approach of Utilizing Water-Soluble Carbohydrates in Lignocellulose Feedstock for Promotion of Cellulosicl-Lactic Acid Production. *J. Agric. Food Chem.* **2018**, *66*, 10225−10232.

(6) Digman, M. F.; Shinners, K. J.; Casler, M. D.; Dien, B. S.; Hatfield, R. D.; Jung, H.-J. G.; Muck, R. E.; Weimer, P. J. Optimizing on-farm pretreatment of perennial grasses for fuel ethanol production. *Bioresour. Technol.* **2010**, *101*, 5305−5314.

(7) Cui, Z.; Shi, J.; Wan, C.; Li, Y. Comparison of alkaline- and fungi-assisted wet-storage of corn stover. *Bioresour. Technol.* **2012**, *109*, 98−104.

(8) Tenorio, C.; Roque, R. Evaluation of different approaches for the drying of lignocellulose residues. *BioResources* **2012**, *7*, 3500−3514.

(9) Liu, Z.-H.; Qin, L.; Jin, M.-J.; Pang, F.; Li, B.-Z.; Kang, Y.; Dale, B. E.; Yuan, Y.-J. Evaluation of storage methods for the conversion of corn stover biomass to sugars based on steam explosion pretreatment. *Bioresour. Technol.* **2013**, *132*, 5−15.

(10) Mujumdar, A. S.; Law, C. L. Drying Technology: Trends and Applications in Postharvest Processing. *Food Bioprocess Technol.* **2010**, *3*, 843−852.

(11) Karlen, D. L.; Birell, S. J.; Hess, J. R. A five-year assessment of corn stover harvest in central Iowa, USA. *Soil Tillage Res.* **2011**, *115-116*, 47−55.

(12) Lin, T.; Rodríguez, L. F.; Shastri, Y. N.; Hansen, A. C.; Ting, K. C. Integrated strategic and tactical biomass-biofuel supply chain optimization. *Bioresour. Technol.* **2014**, *156*, 256−266.

(13) Lu, X.; Withers, M. R.; Seifkar, N.; Field, R. P.; Barrett, S. R. H.; Herzog, H. J. Biomass logistics analysis for large scale biofuel production: case study of loblolly pine and switchgrass. *Bioresour. Technol.* **2015**, *183*, 1−9.

(14) Joseph, E. C.; Satish, V. J.; Bruce, E. D. Technical and Financial Feasibility Analysis of Distributed Bioprocessing Using Regional Biomass Pre-Processing Centers. *J. Agric. Food Ind. Organ.* **2007**, *5*, 1−29.

(15) Lynd, L. R.; Laser, M. S.; Bransby, D.; Dale, B. E.; Davison, B.; Hamilton, R.; Himmel, M.; Keller, M.; McMillan, J. D.; Sheehan, J.; Wyman, C. E. How biotech can transform biofuels. *Nat. Biotechnol.* **2008**, *26*, 169−172.

(16) Yang, B.; Wyman, C. E. Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels, Bioprod. Biorefin.* **2008**, *2*, 26−40.

(17) Palmqvist, E.; Hahn-Hägerdal, B. Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification. *Bioresour. Technol.* **2000**, *74*, 17−24.

(18) Klinke, H. B.; Thomsen, A. B.; Ahring, B. K. Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass. *Appl. Microbiol. Biotechnol.* **2004**, *66*, 10−26.

(19) Zhang, J.; Shao, S.; Bao, J. Long term storage of dilute acid pretreated corn stover feedstock and ethanol fermentability evaluation. *Bioresour. Technol.* **2016**, *201*, 355−359.

(20) Lloyd, T. A.; Wyman, C. E. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresour. Technol.* **2005**, *96*, 1967−1977.

(21) Kim, J. S.; Lee, Y. Y.; Kim, T. H. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresour. Technol.* **2016**, *199*, 42−48.

(22) Ko, J. K.; Kim, Y.; Ximenes, E.; Ladisch, M. R. Effect of Liquid Hot Water Pretreatment Severity on Properties of Hardwood Lignin and Enzymatic Hydrolysis of Cellulose. *Biotechnol. Bioeng.* **2015**, *112*, 252−262.

(23) Konda, N.; Shi, J.; Singh, S.; Blanch, H. W.; Simmons, B. A.; Klein-Marcuschamer, D. Understanding cost drivers and economic potential of two variants of ionic liquid pretreatment for cellulosic biofuel production. *Biotechnol. Biofuels* **2014**, *7*, 86.

(24) Bals, B. D.; Dale, B. E. Developing a model for assessing biomass processing technologies within a local biomass processing depot. *Bioresour. Technol.* **2012**, *106*, 161−169.

(25) Lamers, P.; Roni, M. S.; Tumuluru, J. S.; Jacobson, J. J.; Cafferty, K. G.; Hansen, J. K.; Kenney, K.; Teymouri, F.; Bals, B. Techno-economic analysis of decentralized biomass processing depots. *Bioresour. Technol.* **2015**, *194*, 205−213.

(26) Lau, M. W.; Bals, B. D.; Chundawat, S. P. S.; Jin, M.; Gunawan, C.; Balan, V.; Jones, A. D.; Dale, B. E. An integrated paradigm for cellulosic biorefineries: utilization of lignocellulosic biomass as self-sufficient feedstocks for fuel, food precursors and saccharolytic enzyme production. *Energy Environ. Sci.* **2012**, *5*, 7100−7110.

(27) Zhang, J.; Wang, X.; Chu, D.; He, Y.; Bao, J. Dry pretreatment of lignocellulose with extremely low steam and water usage for bioethanol production. *Bioresour. Technol.* **2011**, *102*, 4480−4488.

(28) He, Y.; Zhang, J.; Bao, J. Dry dilute acid pretreatment by co-currently feeding of corn stover feedstock and dilute acid solution without impregnation. *Bioresour. Technol.* **2014**, *158*, 360−364.

(29) Shao, S.; Zhang, J.; Hou, W.; Qureshi, A. S.; Bao, J. Lower pressure heating steam is practical for the distributed dry dilute sulfuric acid pretreatment. *Bioresour. Technol.* **2017**, *238*, 744−748.

(30) Liu, G.; Zhang, Q.; Li, H.; Qureshi, A. S.; Zhang, J.; Bao, X.; Bao, J. Dry biorefining maximizes the potentials of simultaneous saccharification and co-fermentation for cellulosic ethanol production. *Biotechnol. Bioeng.* **2018**, *115*, 60−69.

(31) Liu, G.; Bao, J. Constructing super large scale cellulosic ethanol plant by decentralizing dry acid pretreatment technology into biomass collection depots. *Bioresour. Technol.* **2019**, *275*, 338−344.

(32) Sluiter, A.; Hames, B.; Scarlata, C.; Sluiter, J.; Templeton, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; National Renewable Energy Laboratory (NREL) Technical Report NREL/TP-510-42618; NREL: Golden, CO, 2012.

(33) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C. *Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples*; National Renewable Energy Laboratory (NREL) Technical Report NREL/TP-510-42623; NREL: Golden, CO, 2008.

(34) Hoover, A. N.; Tumuluru, J. S.; Teymouri, F.; Moore, J.; Gresham, G. Effect of pelleting process variables on physical properties and sugar yields of ammonia fiber expansion pretreated corn stover. *Bioresour. Technol.* **2014**, *164*, 128−135.

(35) Qiu, H.; Sun, L.; Xu, X.; Cai, Y.; Bai, J. Potentials of crop residues for commercial energy production in China: A geographic and economic analysis. *Biomass Bioenergy* **2014**, *64*, 110−123.

(36) Xing, A.; Liu, G.; Wang, Y.; Wei, F.; Yong, J. E. Energy and Environment Analysis on Biomass Collection Process. *Chin. J. Process Eng.* **2008**, *8*, 305−313. (in Chinese)

(37) Adney, B.; Baker, J. *Measurement of Cellulase Activities*; Natinaol Renewable Energy Laboratory (NREL) Analytical Procedure (LAP)-006; NREL/TP-510-42628; NREL: Golden, CO, 1996.

(38) Ghose, T. K. Measurement of cellulase activities. *Pure Appl. Chem.* **1987**, *59*, 257−268.

(39) Bradford, M. M. A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal. Biochem.* **1976**, *72*, 248−254.

(40) Han, X.; Bao, J. General Method to Correct the Fluctuation of Acid Based Pretreatment Efficiency of Lignocellulose for Highly Efficient Bioconversion. *ACS Sustain. Chem. Eng.* **2018**, *6*, 4212−4219.

(41) Zhang, J.; Zhu, Z.; Wang, X.; Wang, N.; Wang, W.; Bao, J. Biodetoxification of toxins generated from lignocellulose pretreatment using a newly isolated fungus, Amorphotheca resinae ZN1, and the consequent ethanol fermentation. *Biotechnol. Biofuels* **2010**, *3*, 26.

(42) He, Y.; Zhang, J.; Bao, J. Acceleration of biodetoxification on dilute acid pretreated lignocellulose feedstock by aeration and the consequent ethanol fermentation evaluation. *Biotechnol. Biofuels* **2016**, *9*, 19.

(43) Brown, L., Torget, R. *Enzymatic Saccharification of Lignocellulosic Biomass*; Natinaol Renewable Energy Laboratory (NREL) Analytical Procedure (LAP)-009; NREL: Golden, CO, 1996.

(44) Li, H.; Wu, M.; Xu, L.; Hou, J.; Guo, T.; Bao, X.; Shen, Y. Evaluation of industrial S accharomyces cerevisiae strains as the

chassis cell for second-generation bioethanol production. *Microb. Biotechnol.* **2015**, *8*, 266−274.

(45) Li, H.; Wu, M.; Xu, L.; Hou, J.; Guo, T.; Bao, X.; Shen, Y.; Bao, X. Evaluation of industrial S accharomyces cerevisiae strains as the chassis cell for second-generation bioethanol production. *Microb. Biotechnol.* **2015**, *8*, 266.

(46) Zhang, J.; Bao, J. A modified method for calculating practical ethanol yield at high lignocellulosic solids content and high ethanol titer. *Bioresour. Technol.* **2012**, *116*, 74−79.

(47) Gu, H.; Zhang, J.; Bao, J. High tolerance and physiological mechanism ofZymomonas mobilisto phenolic inhibitors in ethanol fermentation of corncob residue. *Biotechnol. Bioeng.* **2015**, *112*, 1770−1782.

(48) Liu, H.; Jiang, G.; Zhuang, H.; Wang, K. Distribution, utilization structure and potential of biomass resources in rural China: With special references of crop residues. *Renewable Sustainable Energy Rev.* **2008**, *12*, 1402−1418.

(49) Hess, J. R.; Wright, C. T.; Kenney, K. L. Cellulosic biomass feedstocks and logistics for ethanol production. *Biofuels, Bioprod. Biorefin.* **2007**, *1*, 181−190.

(50) Brand, M. A.; Muñiz, G. I. B. d.; Quirino, W. F.; Brito, J. O. Influence of storage time on the quality of biomass for energy production in humid subtropical regions. *Cerne* **2010**, *16*, 531−537.

(51) Nuemi, J. The effect of whole-tree storage on the fuelwood properties of short-rotation Salix crops. *Biomass Bioenergy* **1995**, *8*, 245−249.