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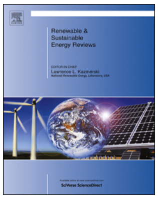

Big bluestem as a bioenergy crop: A review

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ABSTRACT

Big bluestem (*Andropogon gerardii*) is an ecologically dominant warm-season (C4) perennial native grass that comprises as much as 80% of the plant biomass in prairies in the grasslands of the North American Midwest. Ranchers adopted the species as a forage crop long ago, but its high cellulosic content and low agricultural input requirements recently have made big bluestem a promising feedstock for ethanol production and bio-oil. The objective of this paper is to review big bluestem's potential as a bioenergy crop with respect to both biology and conversion. Biology includes distribution and adaptation of big bluestem, ecotypes and varieties currently studied, production management, and disease and pest control. Conversion includes discussion of the conversion of big bluestem biomass to bio-ethanol and bio-oil. Estimated ethanol yield of big bluestem is about 1886 L/ha, which is comparable to previously reported herbaceous biomasses. Various constraints and potential applications of big bluestem as an energy crop are analyzed in the final section of this paper. Plant breeding research that focuses on modifying big bluestem composition to minimize recalcitrance to bioconversion and increasing biomass yields is imperative.

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1. Introduction

1.1. Energy shortage and environmental benefits

Renewable fuels derived from biomass could decrease our dependence on fossil fuel resources and reduce greenhouse gas emissions [1]. First-generation biofuel produced from starch-based and sugar-based biomass is not sustainable because of competition with food crops and insufficient land availability [2]. Therefore, lignocellulosic biomass, including dedicated energy crops such as big bluestem, switchgrass, forest residues, and agricultural residues, could effectively supplement biofuel production because they require low production inputs and less competition with food production.

The Biomass Research and Development Technical Advisory Committee (formed to advise the United States [US] Department of Energy [DOE] and the US Department of Agriculture on program priorities as part of the US Biomass Research and Development Act of 2000 [3]) set a national goal for biomass to supply 5% of total industrial and electric generation energy demand, 20% of transportation fuel consumption, and 25% of bio-based chemicals and materials by 2030 [3], requiring an annual supply of 907 million Mg (1 billion dry tons) of biomass. Approximately one-third of this biomass is projected to originate from perennial crops such as big bluestem and switchgrass. Achievement of this goal requires significant technological advances in plant breeding, biology, agronomy, and conversion technologies [4,5].

Table 1
Species screened by the DOE Herbaceous Crops Program (1986–1992) [10].

Species	Institution and year of project start						
	VA Tech 1985	**Auburn** 1985	**Geophytes** 1985	**Cornell** 1985	**Purdue** 1985	**ISU**[a] 1988	**NDSU**[b] 1988
Grasses: perennial							
Big bluestem (w)					X	X	
Bahiagrass (w)		X					
Bermudagrass (w)		X[c]					
Crested wheatgrass (c)							X
CRP mixture of grasses (c/w)							X
Eastern gamagrass (c)				X			
Energy cane (w)		X					X
Intermediate wheatgrass (c)							
Johnsongrass (w)		X[c]					
Napiergrass (w)							
Redtop (c)				X			
Reed canarygrass (c)			X	X	X[d]	X	X
Smooth bromegrass (c)							X
Switchgrass (w)	X	X	X	X	X	X	X
Tall fescue (c)	X	X	X		X[d]		
Timothy (c)/redtop (c)/clover			X	X			
Weeping lovegrass (w)	X				X		
Wheatgrass mixture (c)							X
Grasses: annual							
Corn (w)		X	X		X	X	
Pearl millet (w)		X[c]					
Foxtail millet (w)							X
Rye (c)		X[e]	X[e]		X[e]	X[e]	
Sorghum, forage (w)			X			X	
Sorghum, sweet (w)		X[c]			X	X	
Sorghum × sudangrass (w)	X				X	X	
Sudangrass (w)				X			
Legumes: annual							
Soybeans						X	
Legumes: perennial							
Alfalfa			X	X[f]	X	X[g]	X[f]
Birdsfoot trefoil	X		X		X	X	
Crownvetch	X						
Flatpea	X			X			
Serecia lespedeza	X	X			X		
Sweet clover				X			
Other							
Forage brassica				X			
Kale				X			
Meadow (mixed grasses and legumes)				X			

Note: Grasses are designated as cool-season (c) or warm-season (w) crops.

[a] ISU = Iowa State University.

[b] NDSU = North Dakota State University.

[c] These crops were frequently the base species in double-cropping or intercropping systems.

[d] Reed canary grass and tall fescue were grown alone and interseeded with sorghum.

[e] Rye was always interseeded among other species or as the cool-season species in a double-crop system, most often with sorghums.

[f] Alfalfa was intercropped with bromegrass at Cornell and NDSU and grown alone at NDSU.

[g] Alfalfa was intercropped with sorghum and sorghum × sudangrass.

The conversion of perennial grasses to biofuels may offer environmental benefits, including increased soil health, reduced losses of soil nutrients, recycling of nutrients from municipal and agricultural wastes, sequestration of soil carbon, and mitigation of greenhouse gas emissions [6–8].

1.2. Historical study of big bluestem as a bioenergy crop in the United States

The Herbaceous Energy Crops Research Program (HECP), one of three energy feedstock research programs supported by the US DOE, was established in 1984. This program focuses on evaluating the best non-woody species and suitability of geographical regions for different types of energy crops. The overall goal of the HECP was to develop data and information that will lead to commercially viable systems in order to produce herbaceous biomass for fuels and energy feedstocks for specific geographical regions. Oak Ridge National Laboratory (ORNL) conducted field management studies and reported that big bluestem could be produced economically on various sites and incorporated into conventional farming operations in various geographical regions [9]. Six universities (Cornell University, Virginia Polytechnic Institute and State University, Auburn University, Purdue University, Iowa State University, and North Dakota State University) and one private company (Geophyta) were selected to participate in the evaluation of 35 potential herbaceous crops, 18 of which were perennial grasses, including big bluestem (Table 1) [10]. At Purdue University, big bluestem and several other herbaceous crops were tested under five levels of fertilizer in both normal and drought conditions from 1985 through 1989 at four sites. Big bluestem yielded 6.8–9.7 Mg/ha, which was similar to other perennial crops [11]. Anderson et al. [12] from Iowa State University tested six herbaceous crops with mono-crop, double-crop, rotating-crop, and inter-crop combinations at various fertilizer levels at two sites (good cropland and marginal cropland) from 1988 through 1992. Big bluestem showed better ability to establish compared to reed canarygrass in marginal land in 1988; biomass yielded 5.5–29.7 Mg/ha. The 29.7M g/ha yield was the highest among all the grasses evaluated and was almost five times higher than switchgrass grown under the same conditions. Anderson et al. also conducted economic analysis that showed big bluestem competed well with switchgrass, with an average cost of $33.13/dry Mg i9n good cropland and $35.33/dry Mg in marginal land [13]. In addition, a grass breeding program led by Viands (approximately 16,000 individual plants transplanted from germinated seeds collected from the Northeast) was implemented to develop big bluestem varieties and other grasses as dedicated bioenergy feedstocks. Big bluestem cultivars and other warm season grass species did not establish as well as the majority of switchgrass cultivars [14].

However, big bluestem has not been adequately explored as biofuel feedstock in regards to ranking with switchgrass and indiangrass, the other two of the “big three” that comprise the greatest percentage of species found in tallgrass prairies in North America [15]. Utilization of big bluestem as biofuel feedstock is strongly motivated by the following: (1) *Big bluestem is a widespread and highly productive tall grass.* This native perennial warm season (C4) tall grass dominates in most native Central US grasslands and produces as much as three times the biomass as switchgrass in native unmanaged grasslands [16]. Consequently, big bluestem can potentially minimize inputs required for annual bioenergy crops, such as re-planting, while advantageously utilizing its ecological competitiveness in grasslands, including growth on marginal lands [17]. (2) *Big bluestem has a robust root system and stores carbon (C) below ground.* Big bluestem establishes easily from seed, spreading vigorously by vegetative growth of underground rhizomes while sequestering large amounts of C in fibrous roots [18] and reducing soil erosion. (3) *Big bluestem has high productivity with few inputs.* Due to its high water and nutrient use efficiency, big bluestem produces more biomass with fewer resources compared to switchgrass [19]; therefore, growth of big bluestem may reduce fertilizer inputs and irrigation. (4) *Big bluestem maintains diversity and wildlife.* Bluestem prairie offers a range of ecosystem services such as wildlife habitat [20], cattle grazing, hay, and pasture lands [21]. (5) *Big bluestem thrives on marginal lands.* Millions of acres of marginal lands have been taken out of row crop agriculture and converted to Conservation Reserve Program (CRP) lands [2]. CRP grasslands could be used for low input, sustainable feedstock in order to avoid competition with crops [22]. (6) *Big bluestem biofuel potential equals or exceeds switchgrass based on several studies* [23–28].

2. Biology

2.1. Description, distribution, and adaptation

Big bluestem (*Andropogon gerardii*) is an ecologically dominant warm-season (with a C4 photosynthetic pathway) perennial native grass that comprises as much as 80% of the plant biomass in prairies in the grasslands of the North American Midwest [29,30]. Big bluestem is in the grass family *Poaceae* and belongs to the *Panicoideae* subfamily and the *Andropogoneae* tribe. Big bluestem plants are often glaucous; clumps are robust and often grow in large tufts, sometimes with short rhizomes. Plants are 1–2 m tall, usually sparingly branching toward the summit; lower sheaths and blades are sometimes villous, occasionally densely so, and the blades are flat, elongated, and mostly 5–10 mm wide with scabrous margins. Racemes on the long-exerted terminal typically produce 3–6 peduncles (fewer on the branches), and they are 5–10 cm long and usually purplish but sometimes yellowish with straight rachis. The joints and pedicels stiffly ciliate on one or both margins, and joints are hispid at the base. The sessile spikelet is 7–10 mm long, the first glume is slightly sulcate and usually scabrous, and the 1- to 2-cm-long awn geniculates and tightly twists below. The pedicellate spikelet is not reduced or is reduced only slightly and is awnless and staminate [18]. Roots of big bluestem may reach depths of 2–4 ft at the end of the establishment year. Roots of well-established plants may reach depths of 7–8 ft [31].

Big bluestem tillers profusely (> 150–200 tillers per plant), with the number depending on the variety or cultivar and growing conditions. Each tiller produces about 10–15 leaves. Tillers that produce inflorescence generally have greater numbers of leaves. Each vegetatively reproductive tiller may have 3–6 adventitious

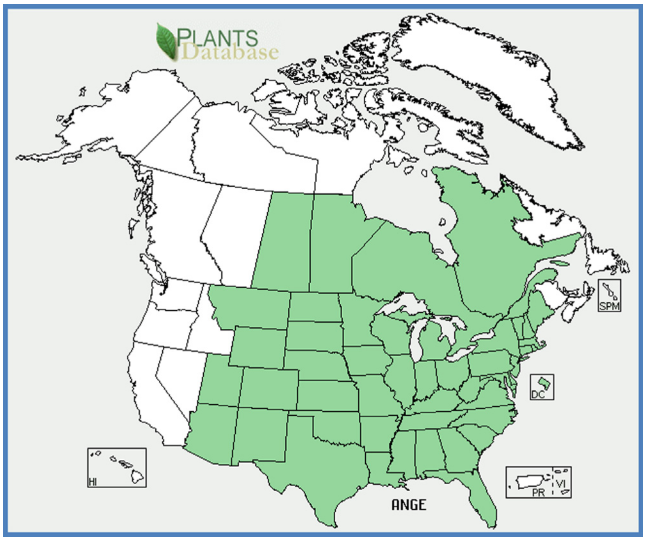

Fig. 1. Big bluestem distribution from the USDA-NRCS PLANTS Database.

roots per rhizome that are confined to the bud-producing and storage portion of the rhizomes [18]. Roots generally emerge after at least one aerial leaf has fully expanded. Most adventitious roots are produced during late summer and early fall and cease initiating roots when tillers stop growing. Each mature, vegetatively reproductive tiller produces 6–14 buds in an alternating arrangement along both sides of its rhizome between stalk structure and culm [18]. Vegetatively non-reproductive tillers usually develop from buds near the aerial culm-base and produce leaves and rudimentary buds but not mature buds or aerial culms. These vegetatively non-reproductive tillers usually die by the end of the season.

Inflorescence of big bluestem consists of 2–6 branched recemes. The shape of these recemes resembles the foot of a turkey, so big bluestem is commonly called “turkey foot” grass. Big bluestem also has a distinct blue coloration at the base toward the culm. Inflorescence typically consists of 3–7 recemes that bear paired spikelets approximately 1 cm long. Similar to many other grass (e.g., traditional sorghum lines) or legume (e.g., soybean genotypes) species, photoperiod determines the time or duration to flower in big bluestem. Big bluestem is a short-day plant, and flowering is triggered when day length starts to decrease. Because big bluestem is highly sensitive to photoperiod and requires a specific photoperiod for flowering, when genotypes from the South are planted in northern regions and exposed to a longer-than-normal photoperiod due to latitude difference, they remain vegetative longer and produce more forage. In contrast, if genotypes from northern regions are planted in southern regions and exposed to shorter photoperiods, they flower and mature early [18]. Flowering typically occurs from July through October. Seed production is critical for reproduction of any plant species. Big bluestem is *andromonoecious* that produces bisexual and male flowers on the same plant. Big bluestem is a self-incompatible species and is cross-pollinated by wind. Pollen dispersal occurs early in the morning, and fertilization is complete within 6–12 h after pollination. Most big bluestem genotypes have chromosome numbers $2\ n = 60$ [18].

Big bluestem is widely distributed in the US, Canada, and Mexico, as shown in Fig. 1. It also adapts well to low soil nutrient and moisture contents and can produce most of its growth during the summer season. It is relatively tolerant to high temperatures and drought stress and performs well in poor-textured soils with low fertility. A recent analysis indicated that more than 25 million hectares of land classified by the USDA as rangeland/grassland within land capability class 3–6 soils (more marginal/less productive soils) could be utilized for bioenergy crop production in select states in the central Great Plains (Kansas, Nebraska, Oklahoma, and South Dakota) [32]. Big bluestem is adaptable in most native prairie ecosystems and represents three times the biomass of switchgrass in midwestern grasslands [16]. Big bluestem productivity is high due to efficient nutrition utilization; it produces twice the biomass per applied N compared to switchgrass and indiangrass [18], it establishes easily from seed, and it spreads vigorously by vegetative growth of underground rhizomes with a robust root system [33]. In addition to economic considerations, bluestem prairie serves a range of purposes in the ecosystem by providing wildlife habitat, cattle grazing, and hay and pasturelands [20].

Table 2
Summary of cultivar, variety, and ecotype of big bluestem.

Variety	Origin of materials
Bison	Central North Dakota
Bonilla	East central South Dakota
Rountree	West central Iowa
Kaw	East central Kansas
Pawnee	Pawnee County, Nebraska
Hampton Germplasm	Arkansas, Missouri, and Oklahoma
OZ-70 Germplasm	Arkansas, Missouri, and Oklahoma
Refuge Germplasm	Arkansas
Northern MO Germplasm	North Missouri
PI 9083274	Logan County, Arkansas
PI 483446	South central Kansas and eastern Oklahoma
Bonanza	Derived from Pawnee
Goldmine	Derived from Kaw
Niagara	Elma, New York
Goldstrike	Nebraska
Champ	Nebraska and Iowa
Earl	Texas
Chet	Texas
Fults	Fult's Hill, Illinois
Walters	Walters, Illinois
DeSoto	DeSoto, Illinois
12miles	Illinois
Carnahan	Carnahan, Kansas
Konza	Konza, Kansas
Tallgrass	Tallgrass, Kansas
Top of the World	Top of the World, Kansas
Webster	Webster, Kansas
Saline	Saline, Kansas
Cedar Bluff	Cedar Bluff, Kansas

2.2. Ecotypes and varieties currently studied

As big bluestem evolved across North America, natural selection in each locale produced a hypothetically unique gene to adapt to specific environmental conditions. In addition, breeders have collected seeds and reproduced them to evaluate their particular genetic and morphological characteristics as well biomass yield, quality, and adaptability. Strains with uniformity are registered as cultivar, ecotypes, or varieties (Table 2).

In recognition of the critical importance of feedstocks to the development of biomass systems, studies of big bluestem have been extensive. Waller and Lewis [34] studied the relationship between latitude of origin and variety yield. Southern varieties of big bluestem that migrated north had higher biomass yield due to extended photoperiods and longer vegetative growth. Previous ecotype studies have provided extensive information regarding agriculture, plant breeding, and restoration ecology [35] and broadened understanding of plant population structure and dynamics [36]. Mintenko evaluated different ecotypes of native grasses for their turfgrass potential under three mowing heights across the northern Great Plains region [37]. Etterson correlated climate change with the evolutionary potential of prairie legumes by investigating three populations in three environments across a broad latitudinal range in the Great Plains [38]. The big bluestem ecosystem has been studied extensively for decades to determine climate’s effects on grass growth; controls on community structure; ecological responses to grazing, burning, and mowing; and restoration effectiveness [16,39–43]. Big bluestem has been a model species for prairie ecology for nearly 100 years, and ecotypes of A. *gerardii* were originally described nearly 50 years ago [44]. McMillan planted six big bluestem ecotypes along a latitudinal gradient in the US in Austin, Texas, and found that the northern ecotypes produced fewer flowering culms than the southern ecotypes [45] and that southern ecotypes had earliest spring activity, latest flowering, and latest dormancy [46]. Johnson et al. recently investigated the genotypic and environmental contribution to observed phenotypic variation of big bluestem using a reciprocal common garden design across the precipitation gradient at three sites. The westernmost ecotype exhibited drought-adapted features with dwarfed stature and significantly reduced canopy area, thus reducing transpiration water loss. The group's data demonstrated strong planting site and ecotype effects as well as interaction between ecotype and planting site [47]. Delucia et al. studied the effects of soil temperature on big bluestem growth. Total big bluestem biomass and relative growth

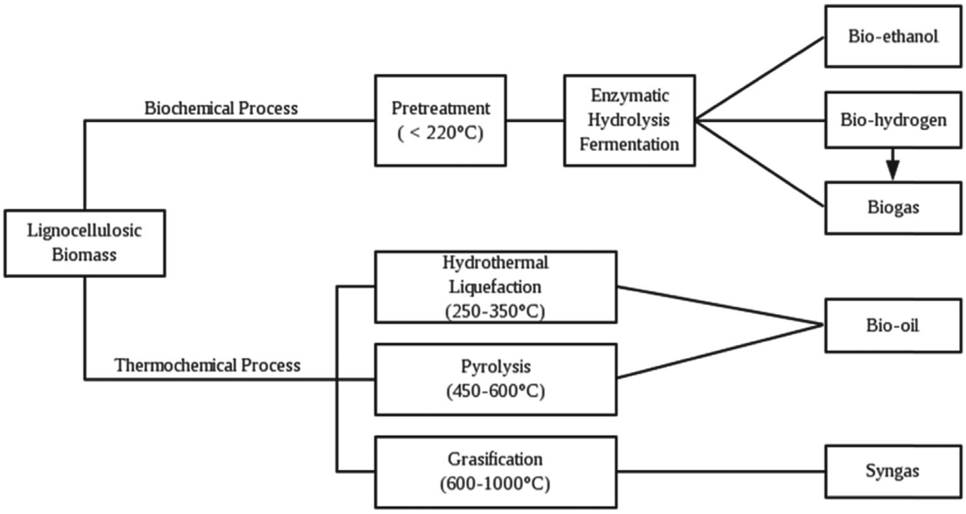

Fig. 2. Major routes for biofuel conversion.

rate (RGR) were maximized at a soil temperature of 25 °C. Both biomass yield and RGR decreased at higher and lower temperatures, and soil temperature did not have a significant effect on leaf area ratio [48].

2.3. Establishment and management

Big bluestem seeds typically are collected in September and October when the seed heads are mature and do not have a creamy center. The collected seeds are dried for 2–4 weeks. At 10 °C and 50% humidity, seeds can be stored up to 7 months. Seedlings can be grown under greenhouse conditions then transplanted or direct-seeded under field conditions. In greenhouse conditions, moist soil should be used to fill germination trays or pots and compacted at the bottom of the containers. Germination uniformity may improve in cold stratification (4.4 °C, 35% humidity), where seeds are exposed to cold temperatures. The seeds should be sown by hand, covered with a thin layer of soil, and kept evenly moist during germination. Fertilizer is not necessary unless the soil is very poor or sandy. The best temperature for germination is alternating day/night temperatures (set at 24/18 °C and 12–14 daylight hours, which may be extended artificially). Seeds generally germinate within a few days and should be allowed to grow and establish for a few weeks. Seedlings should then be transplanted into plug cells; this stage does not require moist soil. Plugs should be moved to a cold frame in early to late spring. When the plant and soil can be completely pulled from the pot as one unit, seedlings are ready for outplanting, which can occur from late May to early October [49].

Direct seeding is more common than transplanting because of the time required to plant large acreages. The direct seeding rate also depends on the planting method. The general recommendation for broadcasting pure-line seed is about 8–10 pounds per acre; if drilled, 6–8 pounds per acre is the correct amount. From late winter through early spring, seeds should be sown directly outside with several irrigations. Emergence occurs in 4 weeks. Big bluestem establishment in a new area depends on seedling performance. Ensuring seedling performance and weed control is necessary to obtain a strong stand in a new area. Big bluestem is tolerant of most of herbicides that control broadleaf weeds. Masters [50] reported that big bluestem stands were successfully established in three out of four environments evaluated with seedlings at 110 PLS/m^2 and in all environments with seedlings at 220–440 PLS/m^2 in the central Great Plains of North America, where stands developed appropriately in 1987 and 1988 when seeded at 14 and 6 plants/m^2, respectively, on areas treated with atrazine [51]. On two sites, subsequent big bluestem yields were at least 1.2 Mg/ha greater in areas treated with metolachlor than in untreated areas. Atrazine increased big bluestem yields by 1.2 and 2.4 Mg/ha at two other study sites [50]. A small big bluestem research plot demonstrated that biomass yield was not affected by stands when stand frequencies the year after establishment were 40% or greater [52]. A cool-season and warm-season forage grass seedling morphology study found that the *Andropogoneae* species took 3–5 days less than other warm-season grasses and 3–15 days less than cool-season grasses to reach third-leaf emergence [53]. Compared to 25 °C and 30 °C, big bluestem seedling growth dramatically reduces at 20 °C. Crabgrass, switchgrass, Caucasian bluestem, and indiangrass seedling weight at 28 days was higher than the big bluestem seedlings when averaged across temperatures [54]. The optimum day/night growth temperature under a controlled environment was close to 30/22 °C, and the temperature below and above resulted in lower biomass accumulation.

Plants are ready to harvest from midsummer through late fall. First-season growth is often slow, but the rate of rhizomatic regeneration increases in subsequent years. Fire disturbance causes underground rhizomes to re-sprout, but regeneration slows if fire occurs during the summer (active growth stage). Because rhizomes have winter-stores of carbohydrates, regeneration following a springtime fire is much more vigorous; therefore, prescribed burning is a common phenomenon in prairies and the Flint Hills, where proper timing and intervals of burns can improve growth and yield. In general, mid- to late-spring burning is prescribed and can lead to higher harvest yields in fall. Effective burn management also can help increase the composition of big bluestem compared to other grasses. Optimal timing and intervals of burning will depend on the environment and soil conditions.

2.4. Fertilizer

Although big bluestem can be grown in marginal soils with low fertility, it responds to fertilizer application with greater biomass and yield. In a big bluestem study conducted in Iowa, Kaw big bluestem produced over 7 tons/ha when 150 kg N/ha was applied, compared to 4 tons/ha of dry matter with no applied N [55]. In Minnesota, Owsley reported that big bluestem can produce 5–8.7 tons of forage per acre under moderate fertility [31]. In 1978 and 1979, Earl big bluestem yielded 8.2 tons/ac and 13.4 tons/ac of dry matter at El Reno Experiment Station, Oklahoma. During those same years, another line of big bluestem in that location yielded 12.1 tons/ac and 17.5 tons/ac, respectively [31]. Big bluestem also responds well to moderate amounts of P and K, particularly during the establishment years. The plants are sturdy, and poor stands can be overcome through the years by adopting good management practices (fertilizer, grazing, or burning), which big bluestem rewards with large biomass production.

During drought conditions, big bluestem and other C4 grasses may experience decreased and increased total plant N allocation to shoots and rhizomes, respectively. Soil N uptake and carbon assimilation are also limited by water availability. Drought-induced retranslocation may protect plant N from loss to herbivory, fire, and volatilization in these periods [56]. In one study, reserve N exhibited a positive relationship with rate of N fertilization. With the rate of N fertilization, reserve N presented positive relation. Because N accumulated over time, the 80 lb N rate exceeded the plant's needs, whereas the 40 lb rate obtained better forage production. Constituent reserves below those of unburned, non-fertilized pastures were not adversely affected by N loading [57].

2.5. Grazing

Big bluestem can survive substantial grazing. In Oklahoma, a study utilized big bluestem, little bluestem, indiangrass, and switchgrass to dominate pastures. Short-duration rotation or two stocking rates and continuous grazing systems were evaluated. In September, total standing crop and dead standing in the rotation units was significantly higher than in the continuous grazing system. Cassels et al. reported that the stocking rate of live and dead standing crops had significant effects on total standing [58].

Big bluestem is currently used primarily for grazing. Losses due to grazing can be as much as two times greater than burning in the absence of grazing; however, grazing conserves approximately 1 g/m^2/yearr N that otherwise would have been lost as a result of combustion [59]. Grazed big bluestem plants had significantly higher rates of photosynthesis than clipped or control plants in one study [60]. The photosynthesis/transpiration ratio and stomatal sensitivity to humidity indicate that, in a higher-light and lower-moisture environment, leaves of grazed plants may develop better than their clipped counterparts. Big bluestem can survive substantial grazing, but if grazing crops the plant closer than 6–8 in other grass species compete with it. In spring and summer, big bluestem is highly palatable to livestock, but it becomes coarse and less palatable during the fall and winter, thereby discouraging grazing [49].

In addition, big bluestem has been widely used to prevent wind erosion by providing aboveground protection [22]. Rhizomes of big bluestem are typically 1–2 in below the soil surface, although the main roots can extend down to 10 ft. White-tailed deer and bison graze vegetative parts, then songbirds and prairie chickens consume the seeds [20].

2.6. Disease and pests control

Several diseases adversely affect big bluestem. Kernel smut, caused by *Sphacelotheca occidentalis*, is characterized by gall-like structures that replace bluestem seeds. Culm smut caused by *Sorosporium provinciale* converts entire inflorescences into galls containing teliospores. Ergot of big bluestem is caused by *Claviceps purpurea*, and big bluestem leaf rust is caused by *Puccinia andropogonis*. Leaf spot of big bluestem can be attributed to *Phyllosticta andropogonivora* and *Ascochyte brachypodii*. One of the most serious pests of big bluestem is the bluestem seed midge, *Contarinia wattsi*. This insect can reduce seed yields by more than 50%. No effective pest control currently exists for this insect; however, a wasp, *Tetrastiches nebraskensis*, parasitizes the midge in the Midwest [61]. Armyworms also can be a serious problem, particularly in dry years. Efficient chemical controls are available for some diseases and pests, but sufficient care should be taken to determine effective timing, and mixes and should be applied only if populations are above the recommended critical limits for all pests and diseases.

3. Conversion of big bluestem into biofuels

Lignocellulosic biomass can be converted to biofuels through various processes, depending on raw material characteristics and the type of biofuels desired. As shown in Fig. 2, two primary conversion processes are related to bio-ethanol, bio-hydrogen, biogas bio-oil, and syngas: a biochemical process and a thermochemical process. In thermal conversion technologies, direct combustion and co-firing with coal were first utilized for electricity production and were responsible for over 97% of the world's bioenergy production [62]. Pyrolysis has attracted the highest interest because it produces bio-oil, which can be used as a fuel for transportation as well as for stable engines and converted into chemicals such as bio-lime N fertilizer [63]. Biomass gasification has been extensively researched because of its increased efficiency compared to combustion. Torrefaction, another promising thermal process, improves quality terms of heat content, physical properties, and chemical composition for combustion and gasification applications [64].

3.1. Conversion of big bluestem biomass to bio-ethanol

Bio-ethanol derived from lignocellulosic biomass via a biochemical process includes the following steps: pretreatment, enzymatic hydrolysis, and fermentation [65]. Bioethanol from lignocellulosic biomass is considered a viable option because it does not compete with starch-based crops for human food and animal feed; however, pretreatment is required to open the microstructure of biomass for enzymatic hydrolysis, which occurs at higher temperature levels with biological catalysts.

3.1.1. Pretreatment process

Pretreatment is required prior to enzymatic hydrolysis in order to reduce cellulose crystallinity, increase biomass porosity, and improve enzyme accessibility [66]. Successful pretreatment must enhance enzyme efficiency, minimize carbohydrate losses, and inhibit by-product formation. Inhibitory compounds commonly found in hydrolysates include acetic acid, formic acid, levulinic acid, furaldehyde 2-furaldehyde (furfural), 5-hydroxymethyl-2-furaldehyde (HMF), vanillin, syringaldehyde, and conferyl aldehyde [67]. The choice of pretreatment depends on raw material characteristics and the final goal of the process. Physical, physico-chemical, chemical, and biological processes have been studied extensively for the pretreatment of lignocellulosic materials, and detailed descriptions of these processes have been described by Mosier et al. [68], Sun and Cheng [66], and Weil et al. [69]. The following sections briefly describe the major types of pretreatment that have been used for big bluestem research.

3.1.1.1. Physical pretreatment. Physical pretreatment of lignocellulosic biomass typically involves size comminution by milling, pelleting, and extrusion. The goal of milling is to reduce the crystallinity of cellulose fibers in the biomass. Size reduction of lignocelluloses is required to eliminate mass and heat transfer limitations during hydrolysis reactions [70]. The size of resulting materials is typically 10–30 mm after chipping and 0.2–2 mm after milling or grinding [66]. Zhang et al. studied the effects of big bluestem size reduction via knife milling. The study reported that, for large particle sizes (8 mm), the cellulose recovery rate after pretreatment was 12% higher than for smaller particles (1 mm). Moreover, big bluestem particles produced with a large sieve had higher enzymatic hydrolysis efficiency, higher sugar yield, and lower energy consumption than those of smaller particles. These results indicate that proper size reduction is desirable because it causes increased hydrolysis. In general, small particle size gives larger surface area, leading to rapid, efficient transport of catalysts, enzymes, and steam to the biomass. This also allows enzymes in the hydrolysis step to penetrate the biomass and reach the sugar oligomers [71]. However, energy consumption has consistently been observed to increase dramatically as sieve size decreases [74]. In some cases, large particles may positively affect biomass conversion [72]. Several studies have reported that large particle size (8–12 mm) has higher cellulose recoveries when applying steam explosion to grinded herbaceous agricultural waste [73]. In addition to particle size, biofuel conversion efficiency is subject to other factors such raw materials, pretreatment strategies, and enzymatic systems.

The extrusion process is a practical high-throughput physical pretreatment for large-scale operations for biomass conversion because of its cost-effective, fast, and simple process. The main steps in this procedure consist of heating, mixing, and shearing the biomass material, resulting in physical and chemical modifications. These modifications include increases in surface area, specific surface area, pore size, and pore quantity and a decrease in cellulose crystallinity, all of which facilitate enzyme access to cellulose. Screw speed and barrel temperature are the two most important factors responsible for disrupting the lignocellulose structure, causing defibrillation, and shortening the fibers, thus increasing carbohydrate accessibility to enzymatic attack. Moreover, extrusion produces no effluent, resulting in no effluent disposal cost, no solid loss, and no safety issues [72]. Karunanithy and Muthukumarappan [73] examined the effects of extruder parameters and moisture content of big bluestem on sugar recovery from enzymatic hydrolysis. Results indicated that maximum glucose (55.2%), xylose (92.8%), and combined sugar recovery (65.4%) were obtained at a screw speed of 100 rpm, a barrel temperature of 150 °C, 15% moisture content, and a 3:1 compression ratio.

Pelleting is another physical pretreatment method used to agglomerate small particles into larger particles by mechanical or thermal processing. Pelleting of biomass involves size reduction of biomass feedstock, conditioning of the ground biomass by applying heat and/or moisture, and extrusion of ground biomass through a die [74–76]. Theerarattananoon et al. [77] reported that the glucan content of big bluestem increases with increased die thickness and decreases with increased hammer mill screen size. Conversely, xylan content of the big bluestem pellets decreases as die thickness increases and increases as hammer mill screen size increases. Among the three combinations of pelleting conditions, big bluestem pelleting that utilizes a die with thickness of 44.5 mm and a hammer mill screen size of 6.5 mm produced the pellets with the highest sugar yield, the highest durability, and the greatest bulk density of biomass [77].

3.1.1.2. Physico-chemical pretreatment. Two types of physico-chemical pretreatments discussed in literature are CO_2 explosion and extrusion combined with alkali. Carbon dioxide explosion is a biomass pretreatment that uses CO_2 as a supercritical fluid (SC–CO_2) [78]. This technique was developed to adopt lower temperatures than those typically used in steam explosion and to reduce the cost compared to ammonia fiber explosion [79]. Supercritical pretreatment conditions can effectively remove lignin, consequently increasing substrate digestibility. The addition of co-solvents such as ethanol, water, and acetic acid can further improve the delignification process [80]. Supercritical CO_2 has been employed primarily as an extraction solvent, but it is also nonextractive and nonflammable, it recovers easily after extraction, and it is environmentally friendly [81]. In aqueous solution, CO_2 forms carbonic acid, which favors biomass hydrolysis. CO_2 molecules are comparable in size to the molecules of water and ammonia; thus, they can penetrate the small pores of lignocellulose. This mechanism is facilitated by high pressure. After the explosive release of CO_2 pressure, cellulose and hemicelluloses structures are disrupted, and the accessible surface area for enzymatic attack increases. Use of lower temperatures than other pretreatments prevents monosaccharide degradation and the formation of inhibitors. Luterbacher et al. [82] studied the glucose, hemicellulose sugars, and two degradation products from enzymatic hydrolysis after a biphasic mixture of an H_2O-rich liquid (hydrothermal) phase and a CO_2-rich supercritical phase-coexist pretreatment. They found the optimal CO_2–H_2O pretreatment conditions were 200 bar pressure, temperatures of 150–250 °C, and residence times from 20 s to 60 min. Pretreatment at 170 °C for 60 min produced the highest big bluestem glucose yield of 68% [82]. CO_2 explosion has many advantages, but this pretreatment method is not yet economically viable because of lower sugar yield and high cost of high-pressure equipment.

Another interesting study about the optimization of extruder parameters to maximize enzymatic sugar recovery was devoted to the combined effect of alkali soaking and extrusion of big bluestem using a laboratory-scale single crew extruder at various barrel temperatures (45–225 °C) and screw speeds (20–200 rpm). Optimum pretreatment conditions were found at 90 °C barrel temperature, 155 rpm screw speed, 2.0% alkali (NaOH) concentration, and 4 mm particle size. Optimal glucose, xylose, and combined sugar recovery were 90.1%, 91.5%, and 89.9%, respectively [83].

3.1.1.3. Chemical pretreatment. Chemical pretreatment involves the use of ozone, acids, alkali, organic solvents, and peroxides to degrade lignocelluloses and increase their susceptibility to enzymatic cellulose hydrolysis. Acid pretreatment is considered an effective method and has been used extensively on various biomasses to remove hemicellulose to high levels of enzymatic hydrolysis and convert solubilized hemicellulose into fermentable sugars [84]. This method has some limitations, however, such as formation of degradation products, release of potential biomass fermentation inhibitors, and requirement of expensive construction materials [85]. Acid treatment commonly uses sulfuric acid, hydrochloric acid, nitric acid, or phosphoric acid, but dilute sulfuric acid has been studied extensively because it is inexpensive and has proven effective, with up to 80% cellulose conversion efficiency [84]. Theerarattananoon et al. [86] examined dilute sulfuric pretreatment of pelleted and non-pelleted big bluestem for bioethanol production and obtained glucan hydrolysis efficiency from 82% to 90%. Zhang et al. [87] studied the effects of sulfuric acid concentration on pretreatment of big bluestem. The pretreatment was carried out at 160 °C for 40 min using four levels of diluted sulfuric acid (0, 1.0, 1.5, and 2.0% w/v) and 6.0% biomass loading (w/v). Glucan yield was 17.8%, 71.6%, 74.2%, and 69.6%, corresponding to biomass treated with acid concentrations of 0%, 1.0%, 1.5%, and 2.0%, respectively. The 1.5% acid concentration resulted in the highest glucan yield due to relatively high enzymatic hydrolysis efficiency and low glucan loss compared to other concentrations. Acid soaking plus microwave pretreatment at room temperature of big bluestem has been studied by Donepudi [88], who achieved maximum glucose and xylose recoveries of 72.9% and 31.2% at 0.7% acid level. Donepudi also carried out similar pretreatments by combining acid soaking with ultrasonic treatment and obtained maximum glucose recoveries of 27% based on total biomass at 0.7% acid concentration and 10 min processing time.

Alkaline treatment involves the use of sodium hydroxide, liquid ammonia, aqueous ammonia, lime, or other alkalis for pretreatment of lignocelluloses. Alkali treatment swells biomass, decreases polymerization, delignifies lignocelluloses, and increases biomass surface area. In general, the alkaline pretreatment process has been used with relative low temperatures and for long periods of time, usually hours or days. Gould reported that glucose yield of big bluestem increased significantly from 0.131 to 0.361 (g/g starting material) after alkaline hydrogen peroxide pretreatment in 50 mL with 1% H_2O_2 for 24 h at 25 °C with initial reaction pH of 11.5 [89]. Combined alkali-microwave, alkali-ultrasound, and alkali-ozone pretreatment of big bluestem by Donepudi [88] was examined at various alkali levels and processing times. Rajendran and Vivek [90] used acid-catalyzed steam explosion and alkaline peroxidation with 1.5% hydrochloric acid hydrolysis for big bluestem treatment at 120 °C for 30 min with a diluted acid: biomass ratio of 8:1. Then ethanol was fermented using *Saccharomyces cereviseae,* and a maximum ethanol yield of 24.14 g/L and 76.9% fermentation efficiency were achieved. Another alkali pretreatment evaluation was studied by Guragain et al., in which maximum enzymatic hydrolysis yield and ethanol yield were 0.71 g/g and 95%, respectively [91]. Sills and Gossett [92] reported using FTIR to predict saccharification from enzymatic hydrolysis of alkali-pretreated big bluestem. The pretreatments were conducted at four NaOH levels: 0, 5, 10, and 20 g per 100 g big bluestem with 5% (w/w) total solids concentration at 25 °C in batch reactors on a rotary shaker at 200 rpm for 24 h. Glucose conversions of 12%, 22%, 51%, and 61% and xylose conversions of 2%, 12%, 41%, and 53% were achieved.

Ozone treatment utilizes ozone gas treatment to delignify the lignocelluloses. The process removes lignin and hemicelluloses without affecting much of the cellulose, while sparging the ozone gas (generated from the ozone generator) onto the biomass with some degree of moisture. The whole process occurs at ambient temperature and pressure, but not all sparged ozone is utilized for the pretreatment; thus, unused ozone escapes to the atmosphere. This underutilization of ozone adds to the cost of pretreatment. Donepudi [88] observed that acid and alkali pretreatment with ozone pretreatment yields higher sugar recovery for big bluestem than ozone treatment alone.

3.1.1.4. Biological pretreatment. Biological pretreatment is a selective degradation process by microorganisms. Previous studies reported that white-rot fungi has been used to pretreat some biomass such as wood chips [75], wheat straw [76], bermudagrass [77], and soft wood [78]. Biological pretreatments require less energy, and unlike other pretreatment processes, no safety issues are involved. However, these pretreatments are less efficient and difficult to use in large-scale production. To date, biological pretreatment of big bluestem has not been reported in the literature. In order to overcome the three major disadvantages of biological pretreatment (low efficiency, long residence time, and limited scale), a combination of pretreatment strategies may have synergistically enhance hydrolysis potential of big bluestem.

3.1.2. Enzymatic hydrolysis

Enzymatic hydrolysis facilitates the cleavage of glycosidic bonds to deconstruct biomass into fermentable sugars. Enzymatic hydrolysis involves three main enzymes: β-1, 4-endoglucanases (EG), cellobiohydrolysases (CBH) or exo-glucanases, and β-glucosidases (BG). EGs cleave amorphous cellulose at internal sites of cellulose chains; CBHs degrade the crystalline structure of cellulose by attacking it at the chain ends and releasing cellobiose; and BGs, which are active only on cello-oligosaccharides and cellobiose, release glucose monomer units from the cellobiose [93,94]. Previous research reported that microorganisms (*Penicillium capsulatum, Talaromyces emersonii*, and *Aureobasidium pullulans*) can degrade hemicellulose while exhibiting greater efficiency than cellulose because hemicellulose does not have tight crystalline structures [95,96]. Yang et al. [80] summarized the current understanding of key features of pretreated biomass and glycosyl hydrolases that influence sugar release and suggested opportunities to further advance understanding of lignocellulosic bioconversion by newly advanced technologies such as genomics, proteomics, and microscopy.

3.1.2.1. Enzymatic hydrolysis of cellulose. Cellulases are typically used in the enzymatic hydrolysis of cellulose. Enzymatic hydrolysis requires mild conditions (4.5 pH and approximately 50 °C), differing from conventional hydrolysis techniques that use alkaline reagents or concentrated acid. Duff and Murray reported that fungal cellulases have the best potential for commercial-scale use [97]; cellulases are produced by bacterial species such as *Clostridium*, *Cellulomonas*, and *Bacillus* [98]. As a complex system of three enzymes, cellulases act synergistically to hydrolyze cellulose. The three enzyme components are β-glucosidase (EC 3.2.1.21), 1,4-β-D-glucan cellobiohydrolyase (EC 3.2.1.91), and 1,4-β-D-glucan glucanohydrolase (EC 3.2.1.3) [99,100], or endoglucanase, exoglucanase, and cellobiase, respectively.

In order to form glucose, cellobiose, and cellotriose, endoglucanase randomly cleaves cellulose chains. Cellobiose units are released when exoglucanase attacks the nonreducing end of cellulose and cleaves cellobiose units into fermentable glucose units. Because cellobiose accumulation results in cellulase inhibition, most fungal cellulases that must be supplemented exhibit limited β-glucosidase activity [101]. Table 3 summarizes results from previous studies of dosage and hydrolysis conditions of enzymatic hydrolysis for big bluestem.

3.1.2.2. Enzymatic hydrolysis of hemicelluloses. Three main enzymes in the complete hydrolysis of xylan are endo-β-1-4-xylanase, which primarily targets internal β-1-4 bonds between xylose units; exoxylanase, which releases xylobiose units; and β-xylosidase, which releases xylose from xylobiose and short-chain xylooligosachharides [102]. Several ancillary enzymes are responsible for cleaving side-groups, although depolymerization primarily involves α-glucuronidase, α-L-arabinofuranosidase, acetylxylan esterase, p-coumaric acid esterase, and ferulic acid esterase [102].

Penicillium capsulatum and *Talaromyces emersonii* have complete enzyme systems and have been used to degrade xylan [103]. Other microorganisms, such as *Aureobasidium pullulans* and several *Fusarium* species [91,92], have been reported as sources of hemicellulose-degrading enzymes [96]. Bachmann and McCarthy [89] also reported that, in cellulase systems, synergism is exhibited in xylan-degrading systems. Because xylan does not form tight crystalline structures, accessibility to the substrate is easier, but the number of enzymes required for xylan hydrolysis is much greater than for cellulose hydrolysis [104]. No comprehensive effort using hemicellulose-degrading enzymes to optimize hydrolysis of big bluestem has been reported to date.

3.1.3. Fermentation

Supernatant from enzymatic hydrolysis of lignocelluloses can contain hexoses and pentoses if cellulose and hemicellulose are hydrolyzed. Depending on the lignocellulose source, the hydrolysate typically consists of glucose, xylose, arabinose, galactose, mannose, fucose, and rhamnose [105]. Glucose and xylose are the dominant sugars in the mixture. *Saccharomyces cerevisiae* and *Zymomonas mobilis* are capable of efficiently fermenting glucose into ethanol but are unable to ferment xylose. Other yeasts, such as *Pachysolen tannophilus*, *Pichia stipitis*, *Entamoeba coli,* and *Candida shehate,* can ferment xylose into ethanol [106,107]. Du [108], and Hahn-Hagerdal et al. [109] noted the difficulties associated with commercial use of xylose-fermenting yeasts, including low ethanol tolerance, difficulty in optimization of fermentation parameters, and slow rate of fermentation. An alternative approach is to convert xylose into an isomer called xylulose using xylose isomerase [110–112]; xylulose can then be fermented by traditional yeasts. However, Saha [105] found that this approach is not cost-effective and that development of genetically engineered microorganisms capable of fermenting hexoses and pentoses into ethanol should be a priority. *S. cerevisiae* is of particular interest, and recent reviews

Table 3
Cellulose activates and hydrolysis conditions from previous big bluestem studies.

Pretreatment	Enzyme activity	Conditions	Result/yield	Reference
Extrusion+alkali	Cellulase:15 FPU, glucosidase:60 CBU	50 °C, 150 rpm, 72h	90.1% Glucose conversion, 91.5% Xylose conversion	[83]
Alkali	Cellulase:15 FPU, glucosidase:25 CBU	2.5% TS, 50 °C, 130 rpm, 48 h	61% glucose conversion, 53% xylose conversion	[92]
Alkali	Cellic CTec2 and Cellic HTec2 in rate of 9:1	6% TS, 50 °C, 150 rpm, 48 h	0.71% Sugar yield	[91]
Acid	Accellerase 1500	6% TS, 50 °C, 140 rpm, 96 h	78.6% Glucose conversion	[77]
CO_2-H_2O	Cellulase:15 FPU, glucosidase:30 CBU	1% TS, 50 °C, 144 h	68% Glucose yield	[82]
Microwave	Cellulase:15 FPU, glucosidase:60 CBU	50 °C,150 rpm, 72 h	30.1% Glucose conversion, 7.7% Xylose conversion	[88]
Ultrasound	Cellulase:15 FPU, glucosidase:60 CBU	50 °C,150 rpm, 72 h	38.2% Glucose conversion, 4.5% Xylose conversion	[88]
Ozone	Cellulase:15 FPU, glucosidase:60 CBU	50 °C,150 rpm, 72 h	17.7% Glucose conversion, 8.1% Xylose conversion	[88]

detail efforts to improve pentose fermentation using this microorganism [113,114].

In addition to separate hydrolysis and fermentation (SHF), other approaches include direct microbial conversion (DMC) and simultaneous saccharification and fermentation (SSF). DMC utilizes microorganisms that simultaneously produce cellulase to hydrolyze cellulose and ferment the resulting sugars into ethanol. *Clostridium thermocellum* and *Clostridium thermosaccharoliticum* have been used in DMC studies [115], but significant by-product formation and low ethanol tolerance are limitations of this approach. In SSF, enzymatic hydrolysis and fermentation take place in the same vessel. The rationale for this approach is that because cellulase activity is inhibited by glucose, rapid fermentation into ethanol increases the rate and efficiency of the overall process.

An in vitro ruminal (IVR) digestion assay for estimation of ethanol production was first tested with switchgrass, big bluestem, and eastern gamagrass [116]. This method greatly reduces processing time and expense of evaluating potential ethanol yield and fermentability of feedstocks. Eastern gamagrass gave the best fit in a linear regression between gas production from IVR and ethanol production (R^2=0.824). This method, along with the traditional in vitro dry matter digestibility (IVDMD) and in vitro organic matter digestibility (IVOMD) methods, was used in a second study that evaluated eastern gamagrass, big bluestem, and sand bluestem at multiple locations over three years [116]. The authors reported that big bluestem had higher fermentability than eastern gamagrass or sand bluestem, but eastern gamagrass yield (6.0–7.9 Mg/ha) was higher than big bluestem (3.9–4.5 Mg/ha) and sand bluestem (5.9–6.4 Mg/ha). Significant environmental effects on fermentability were present, however, as well as significant varietal differences [116].

3.2. Conversion of big bluestem to gaseous biofuels

Main biorenewable gaseous fuels include biohydrogen and biogas. Hydrogen is an ideal energy source because of its possible greenhouse gas neutrality and clean residues. Although hydrogen can be produced through many conventional and mature methods, such as steam reformation of hydrocarbons, biohydrogen derived from biomass is widely taken into account as an alternative energy for sustainability. The conversion of biomass into biohydrogen is carried out by a series of microorganisms through hydrolysis and anaerobic fermentation (Fig. 3). Biomass is initially digested into soluble monomers or oligomers sugars in a process known as hydrolysis. Fermentative bacteria releases extracellular enzymes to ferment soluble sugars into a mixture of biohydrogen (H_2), carbon dioxide (CO_2), ethanol, and low molecular weight volatile fatty acids (VFAs), such as propionic and butyric acids. H_2 fermented from soluble sugars can accumulate in the system because microorganisms' hydrogen-scavenging activity is relatively weak or absent, thereby producing a maximum of 2 and 12 mol of H_2 from every mol hexose and glucose, respectively [117]. Some of reduced soluble sugars are oxidized to acetate as by-production, even if oxidation provides low partial pressures for enhancing H_2 yield. This process could be completed without hydrogen production due to acetate transformation; however, these kinds of pathways allow less energy for growth and are not used at low partial pressures of hydrogen [118]. Meanwhile acetogenesis oxidized ethanol and VFAs by hydrogen-producing acetogenic bacteria into H_2, acetate, and CO_2 [119]. Although initial biohydrogen research began in the 1980s, hydrogen bioconversion is still subject to extensive research due to some limitations [120]. The major factors affecting hydrogen yield and efficiency include the following: (1) Biomass composition. Although no clear conclusion has been drawn in previous researches, a reasonable hypothesis is that hydrogen yields may be positively correlated to the cellulose while there is negative relationship between lignin contents biomass digest ability [121]. (2) Pretreatment. In order to increase the accessibility of cellulose and hemicellulose, pretreatment to open lignin protection is necessary. Although pretreatment approaches are adaptably conducted based on mechanical, chemical and biological techniques, the goal of pretreatment is to break down the cross link between cellulose, hemicellulos, and lignin in order to favor hydrolysis [122,123]. Table 4 summarizes published data regarding conversion of grass biomass into biohydrogen with varied pretreatment and inoculation methods, although grass biomass with similar composition could significantly differ in hydrogen yield. (3) Operation conditions. Key operational parameters such as low pH, low partial pressure, high temperature, and acclimated microbial communities are recommended. These operating parameters not only affect the yields of biohydrogen in mixed culture, but they also redirect the by-product spectrum and impact the structure of microbial communities [124]. (4) Inoculum

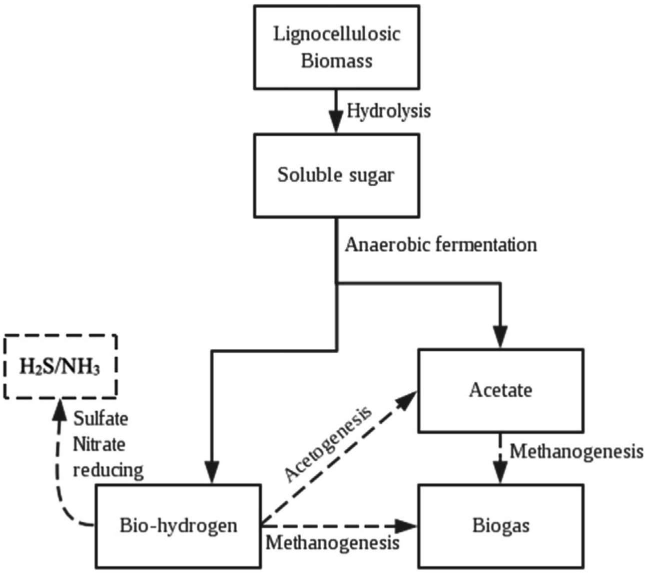

Fig. 3. Anaerobic digestion pathways to produce biohydrogen and biogas, in which bold arrows indicate biohydrogen producing pathways and dotted arrows are biohydrogen consuming pathways.

Table 4
Biohydrogen and biogas production potential of grass biomass feedstock.

Biomass	Pretreatment condition	Inoculum	Gaseous fuels yield	Reference
Miscanthus	12%NaOH(70 °C, 4 h)and commercial enzymes(45 °C, 72 h, pH 4.8)	*T. elfii* DSM 9442	2280 mLH_2	[199]
Lawn grass	4% HCl (30 min, boiling)	Enrichedmixedculture dominated by *C. pasteurianum*	72.21 mLH_2/g DM	[200]
Switchgrass	Untreated	*C. saccharolyticus* DSM 8903	11.2 mmol H_2/g substrate	[201]
Grass silage	Untreated	Meso- and thermophilic bacteria	16.5 mL H_2/g substrate	[118]
Grass silage	Alkaline	Treating cow manure and confectionery by-products	9.9 ml H_2/g VS	[202]
Napier grass	Untreated	Bacterial strains isolated from effluent sludge	6.66H_2 mmol/g substrate	[203]
Bermuda grass	Untreated	Enriched microbial culture	3.5 SCF CH_4/lb VS	[204]
Reed canary grass	3% HCl (90 min,121 °C, autoclave)	Enriched microbial culture	1.25 mmol H_2/g DM and 8.26 mmol CH_4/g DM	[205]
Switchgrass	Steam-exploded	Brewery wastewater	99.86H_2/g VS and 0.5 mL CH_4/g VS	[206]
Switchgrass	Alkalinization and autoclaving	Treating apple wastewater	256.6 8.2 ml CH_4/g VS	[207]
Grass ensilage	Untreated	Isolated microorganism from sludge	0.6–0.7 CH_4Nm^3/kg DM	[119]

DM = dry material.
VS = volatile solids.

strains. Monoculture such as *E. coli* and mixed microorganisms consortia can ferment sugars into hydrogen. Of their advantages, monoculture more effectively prevents contamination that is difficult and costly to maintain out of laboratories. However, mixed microorganisms consortia is favorable in real-case, scaled-up applications due to restrictions of sterility criteria [125]. (5) Bioreactor design. The key consideration of a bioreactor is accumulation of hydrogen from reduced partial hydrogen pressure in the system due to venting hydrogen and sparing inert gas [126,127]. Currently, the most common bioreactor is a completely stirred tank reactor, but up-flow anaerobic sludge blanket, anaerobic membrane bioreactors, and immobilized bioreactors have been emerging due to improved hydrogen yield potential [125]. (6) Hydrogen diversion. Three competitor consuming hydrogen exist: sulfate-reducing bacteria (SRB), methane-producing bacteria (MPB), and homoacetogenic bacteria (HAB) (Fig. 3) [124].

Biogas, a gas mixture primarily consisting of 55–70% CH_4 and 30–45% CO_2, is generated from organic material such as biomass and agricultural residues in the absence of oxygen by a mixed population of microorganisms [128]. Biogas is a clean, renewable alternative energy source that can be used after appropriate gas clean-up as fuel for engines, gas turbines, fuel cells, boilers, industrial heaters, and other processes, or for the manufacturing of chemicals. Biogas technology offers an attractive route to utilize certain categories of biomass for meeting partial energy needs. Unlike other forms of renewable energy, biogas does not have geographical limitations or required technology to produce energy, and it is not complex or monopolistic [129]. Biogas production is competitive pathway with hydrogen conversion in anaerobic digestion. As shown in Fig. 3, H_2 can also be consumed by hydrogen-oxidizing acetogenic bacteria known as acetogenesis for acetate. Acetotrophic and hydrogenotrophic methanogesis convert acetate, H_2, and CO_2 into a mixture of biogas (CH_4) and CO_2. Acetotrophic methanogesis uses acetate as a substrate to produce 70% of total CH_4, while the remaining CH_4 is mostly produced from CO_2, using H_2 as an electron through hydrogenotrophic methanogenesis [130]. Small amounts of CH_4 are also formed from formic, propionic, and butyric acids and from other organic substrates by methanogens [131]. Hydrolysis is considered the rate-limiting step for high-solid feedstocks such as biomass feedstocks; methanogenesis is the rate-limiting step for high soluble [132]. End products are CH_4 and digestate, a moist solid that is typically dewatered to produce a liquid stream and a dry solid [133]. Anaerobic processes utilize a small part (approximately 14%) of the available energy for microbial growth (10% for fermentative bacteria and 4% for methanogenesis); most energy (approximately 86%) is converted into CH_4 as end product [134]. At present, grassland biomass is used in practice as a well-established feedstock for biogas production in Europe and North America due to strong economic viability and positive environmental impact [135,136]. Peochnow et al. [137] reviewed current knowledge of suitability and sustainability of grassland biomass for biogas regarding grassland management, harvest, postharvest, and digestion technology. They reported that grassland management intensity and cutting period have been demonstrated to be of prior importance among the many factors that influence biogas yield [137]. Warm season grasses likely have good potential for biogas applications if effective cultural management and optimized biogas conversion systems are developed. Big bluestem and eastern gamagrass may prove more suitable for this application than switchgrass because they have improved digestibility for livestock [138]. Table 4 summarizes some published results of biogas production from grass biomass. To our best knowledge, no published data exists regarding conversion of big bluestem to biogas. Big bluestem is a valuable grass native to North America, but, compared to switchgrass, it has been understudied as a biogas feedstock.

Commercial application of biogas has been widely disseminated in developing countries since the 1970s, currently with approximately 4 and 27 million biogas plants with typically small systems in rural areas fed by animal manure in India and China, respectively [139]. Nepal has installed over 60,000 biogas plants by1999 [140], while 24,000 biogas plants have been constructed in Bangladesh by 2005 [141]. In Thailand, biogas facilities, with a total capacity of 60210 m^3, have been installed in 2001 [142]. In Latin America, Costa Rica has moderately disseminated biogas plants in 1990s [143]. Akinbami et al. reviewed the number of biogas plants in Africa: Zimbabwe had 100 plants, Burundi had 136 plants, Kenya had 140 plants, and Tanzania had 600 plants [144].

3.3. *Conversion of big bluestem to bio-oil via hydrothermal liquefaction*

Hydrothermal liquefaction (HTL) is a thermochemical conversion technique that uses liquid subcritical water as a reaction medium for the conversion of organic matters to bio-oil, gases, char, and water-soluble matters in a heated, pressurized, and oxygen-absent enclosure [145]. HTL is conducted under elevated pressure (50–200 atm) and low temperature (200–400 °C) to keep water in a liquid or supercritical state. Water serves as reaction medium and reactant, and the process offers several advantages: (1) no need to dry biomass; (2) high energy and separation efficiency; (3) high throughputs; (4) complete sterilization of products from any pathogens, including bio-toxins, bacteria, or viruses; and (5) reduced mass transfer resistance in hydrothermal conditions [146]. When water in HTL is under supercritical conditions and remains in a liquid state, it has a range of exotic properties; when water is close to the critical point, it has low viscosity and high solubility of organic substances, thereby subcritical water is an excellent medium for fast, homogeneous, and efficient reactions [147–149]. Moreover, researchers have reported that many reactions have a high activation volume at subcritical conditions because a high dielectric medium of subcritical water lowers the activation energy of a reaction for a transition state of higher polarity than the initial state [150,151].

The primary product of HTL is an oily, organic liquid called bio-oil (or heavy oil), solid residue (or bio-char), aqueous products (or bio-crude or light oil), and gases. Bio-oil is a viscous, corrosive, unstable mixture of a large number of oxygenated molecules, depending on the pyrolysis process and biomass feedstock. Due to high oxygen content, bio-oil heating value is less than half that of petroleum liquid. Bio-oil must be upgraded before use as a liquid fuel [152] and may serve as starting material for valuable petroleum-based fuels (e.g., gasoline and diesel) and products such as polymers, aromatics, lubricants, and asphalt [146]. Aqueous phase (light oil) reforming processes have been utilized successfully to convert biomass-derived water-soluble carbohydrates to liquid alkanes and hydrogen [153]. The main gaseous products are carbon dioxide and carbon monoxide. In Akalın's study [113], the major components from HTL of cornelian cherry stones were (Z,Z)-9,12-octadecadienoic acid, phenols, and furfurals. Among major identified compounds, the relative concentration of (Z,Z)-9,12-octadecadienoic acid was the highest, which is the main fatty acid product, in addition to palmitic acid (n-hexadecanoic acid) and linoleic acid ((Z,Z)-9,12-octadecadienoic acid), in bio-oils from hydrothermal liquefaction of biomass [154–158].

Bio-crude, the aqueous fraction of products after HTL, can be converted to liquid fuel, hydrogen, or chemicals [63]. Karagoz et al. reported that bio-oils from the hydrothermal treatment of cellulose consisted of furan derivatives, whereas lignin-derived oil contained phenolic compounds [159]. Previous research showed bio-oils derived from corn stover via hydrothermal liquefaction contained phenol, guaiacol, 4-ethyl-phenol, 2-methoxy-4-methyl-phenol, 4-ethylguaiacol, 2,6-dimethoxyphenol, 1,2,4-trimethoxybenzene, 5-tert-butylpyrogallol, 1,10-propylidenebis-benzene, 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone, acetic acid, 1-hydroxy-2-propanone, furfural, 3-methyl-2-cyclopenten-1-one, 2,5-hexanedione, and desaspidinol [160]. Bio-char is similar to that of coal with less fibrous structure and high calorific value, making it an excellent candidate for solid fuel. Bio-char is highly resistant to decomposition upon land application and has a number of positive effects on soil fertility [161]. In addition, the application of bio-char as an effective adsorbent has been studied extensively. The sorption properties of activated carbons are extremely versatile and can be used to remove a variety of inorganic and organic contaminants, such as heavy metals [162], arsenates [163], organic dyes [164], and many other toxic substances [165] from water.

Gan et al. [23] conducted HTL of big bluestem into bio-oil using sodium hydroxide as a catalyst at 1100 psi and 280 °C. The study reported that bio-oil yields of big bluestem were 19.5–27.2%. The bio-oil carbon content was 69.8%–77.9%, and oxygen content was 14.0–22.0%. They also analyzed the effect of ecotype and planting location on bio-oil yield as well as carbon and oxygen content in the bio-oil. The general conclusion of this study indicated that bio-oil yield of big bluestem from HTL was significantly affected by ecotype and planting location, but planting location was most influential. In addition, they found that bio-oil C and O contents were significantly affected primarily by ecotype. The authors suggested that big bluestem and switchgrass have similar potential for bio-oil production via HTL. Another fast pyrolysis biorefinery of big bluestem study reported that bio-oil yield was 71%; the most important constituents, hydroxyacetaldehyde, phenol, and anhydroglucose yields, were 13%, 5%, and 9%, respectively. Both hydroxyacetaldehyde and anhydroglucose yields of big bluestem were approximately 50% higher than switchgrass due to its low potassium content [166]. Tiffany et al. analyzed economic feasibility and indicated that the returns on investment from big bluestem (US $19.38/Mg) exceeded switchgrass (US$10.47/Mg) [167].

3.4. Conversion of biofuel via pyrolysis and gasification

Pyrolysis is the thermal decomposition of materials in the absence of oxygen. In contrast, gasification decays biomass to syngas with controlled amounts of oxygen. The major products from pyrolysis are bio-oil, bio-char, and syngas. General pyrolysis process includes heat transfer from heating medium to biomass, biomass phase change, and gas condensation [168]. During past 20 years, fundamental research on fast or flash pyrolysis has shown that high yields of primary, non-equilibrium liquids and gases from carbonaceous feedstocks, including valuable chemicals, chemical intermediates, petrochemicals, and fuels, can be obtained. Therefore, higher-value fuel gas, fuel oil, or chemicals from fast pyrolysis can replace the lower value solid char from traditional slow pyrolysis [169]. Depending on operating settings, pyrolysis processes are classified as conventional pyrolysis and fast pyrolysis [170]. Conventional pyrolysis may also be called slow pyrolysis. The terms “slow pyrolysis” and “fast pyrolysis” are slightly discretional and have no exact definition of times or heating rates.

Bridgwater and Peacocke [176] summarized key features of fast pyrolysis, and they described the major processes developed over the past 20 years. Bridgwater reviewed the configuration and upgrading of fast pyrolysis design [171,172]. By combustion, gasification, and fast pyrolysis, the technical and economic performances of thermal processes have been assessed to generate electricity from a wood chip feedstock.[171,172]. The fast pyrolysis process design, pyrolysis reactors, current status of pyrolysis processes in various countries, and commercialization were covered by Bridgwater [171,172].

Gasification is partial thermal oxidation, resulting in a high proportion of gaseous products (CO_2, H_2O, CO, H_2 and gaseous hydrocarbons), small quantities of char (solid product), ash, and condensable compounds (tars and oils). In gasification, an oxidizing agent such as steam, air, or oxygen is supplied to the reaction, and the quality of gas produced can be standardized. Compared to the original biomass, it can be used for multipurpose (e.g., powering gas turbines and gas engines or as chemical feedstock for liquid fuel production). By converting syngas into marketable fuels and products, gasification adds value to low- or negative-value feedstock. Many researchers have studied chemistry reactions of biomass gasification, which generally include drying, pyrolysis, oxidation, and reduction [173,174]. Moreover, Rauch has reviewed biomass gasification reactor technologies in small and large scales. The fixed-bed, fluidized-bed, entrained-flow, and stage gasification with physical separation of pyrolysis, oxidation, and/or reduction zones can all be classified by reactor design [175]. Commercial gasification facilities in Europe, the United States, and Canada are approximately 75% fixed-bed downdraft, 20% fluidized-bed systems, 2.5% updraft, and 2.5% of various other designs [176]. To date, no information has been published regarding pyrolysis and gasification of big bluestem. However, big bluestem has similar chemical composition and higher yield potential compared to switchgrass, which has a large number of literatures [177–184].

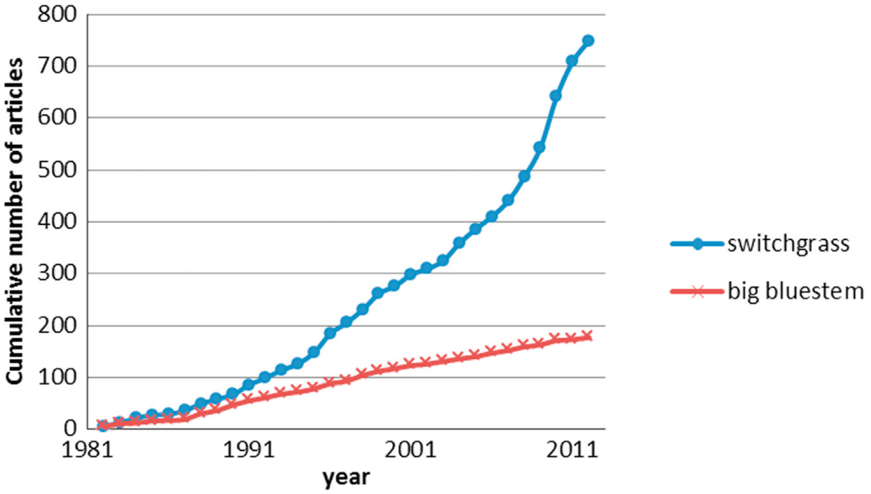

Fig. 4. Cumulative number of articles on switchgrass and big bluestem listed in the AGRICOLA literature database.

4. Potential and future outlook of big bluestem for biofuels

Fig. 4 shows the cumulative number of articles on switchgrass and big bluestem listed in the AGRICOLA literature database from 1981 through 2011. Although our screening effort was limited, the figure indicates that a majority of previous studies investigating herbaceous grasses as energy crops have focused only on analysis of switchgrass during the past two decades. Big bluestem had only one-third the cumulative number of related articles that selected it as a model species, thereby gaining funding support from DOE [9,185].

Several factors suggest sole reliance on switchgrass, but natural, pure stands of big bluestem are more common than switchgrass in the tallgrass prairies of the Midwest. Big bluestem is generally more palatable as hay and grass in the latter part of the season, so producers concerned about long-term options may prefer it [186]. Some landowners also consider switchgrass excessively invasive. Production of ethanol and value-added chemicals via consolidated bioprocessing (a direct fermentation process) indicate that big bluestem is a superior feedstock to switchgrass and eastern gamagrass [116]. Another advantage of big bluestem is that it can produce twice the biomass per unit of applied N compared to switchgrass or indiangrass [33]. In addition, big bluestem is the dominant species in the second year after switchgrass dominates in the first establishment year [187], proving that the proportion of big bluestem increased significantly when it was grown in monoculture or with indiangrass and switchgrass during the second year [188]. Madakadze et al. ranked the average lignocellulose content as cordgrass > big bluestem > switchgrass > sandreed > indinagrass in southwestern Quebec, Canada [189]. Waramit et al. reported that big bluestem tends to contain higher cellulose concentrations than switchgrass [190].

Table 5 summarizes the average cellulose content, hemicellulose content, and biomass yield of big bluestem from previous studies. The average and range of cellulose content, hemicellulose content, and biomass yield were 37.2% with a range of 33.5–49.8%, 23% with a range of 17.7–31.5%, and 7Mg/ha with a range of 3.2–11.4 Mg/ha. The potential ethanol per hectare was calculated by multiplying yield data (kg/ha) based on cellulose content (% of dry biomass), yielding a factor of 1.11 to account for weight gain during hydrolysis because of the addition of a water molecule. During glucose-to-ethanol fermentation, the resulting kilograms of glucose per hectare data points were multiplied by 0.5114 to account for the weight loss of two CO_2 molecules and multiplied by 1.2764 to convert ethanol weight to volume (kilogram to liter). Table 6 compares potential ethanol yields of big bluestem and other selected biomasses. In general, perennial warm-season grass ethanol yields were lower than annual crop yields because the latter had higher biomass yield. The estimated ethanol yield of big bluestem calculated from a previous study was 1886 L/ha, which is comparable to previously reported herbaceous biomasses (switchgrass, miscanthus, and eastern gamagrass). Total estimated ethanol yields followed trends similar to total biomass yields. In addition, big bluestem had similar production costs compared to switchgrass and lower costs compared to alfalfa and reed canarygrass [191]. A comparison of the cost of bio-oil processing showed that big bluestem was less expensive than switchgrass and produced more bio-oil from pyrolysis. The returns on investment from big bluestem (US$19.38/Mg) also exceeded switchgrass (US$10.47/Mg) [167].

Table 5
Average cellulose content, hemicellulose content, and biomass yield of big bluestem from previous studies.

Cellulose content (%)	Hemicellulose content (%)	Yield (Mg/ha)	Reference
NA	NA	6.1	[208]
NA	NA	8.5	[209]
NA	NA	4.5	[210]
NA	NA	8.5	[11]
NA	NA	8.3	[12]
NA	NA	5.5	[211]
NA	NA	11.4	[212]
NA	NA	3.2	[213]
34.7	29.2	NA	[214]
33.1	17.7	NA	[88]
34.5	27.0	NA	[25]
37.9	21.1	NA	[92]
40.1	21.6	NA	[77]
37.6	19.9	NA	[82]
35	18.2	NA	[73]
35.6	20.2	NA	[91]
49.8	31.5	NA	[166]
33.5	23.7	NA	[215]
37.2	23	7	Average of previous study

4.1. Commercialization of biofuel from lignocellulosic biomass

Amigun et al. [192] reviewed commercialization of biofuel in Africa. Africa contains a few operating commercial biofuel systems with small capacity, and existing bioethanol plants are concentrated primarily in the Southern African Development Community, including South Africa, Malawi, Swaziland, Mauritius, Zimbabwe

Table 6
Comparison of potential ethanol yields of big bluestem and other selected biomasses.

Biomass	Potential ethanol yields (L/ha)	Reference
Big bluestem calculated from previous study	1886	Calculated
Kaw big bluestem[a]	1893	[208]
Big bluestem[b]	2602	[209]
Kanlow switchgrass[a]	2070	[208]
Switchgrass[b]	3289	[209]
Miscanthus[a]	2499	[208]
Eastern gamagrass[b]	3019	[209]
Photoperiod-sensitive sorghum[a]	7637	[208]
Sweet sorghum[c]	9920	[208]
Dual-purpose forage sorghum[d]	6516	[208]
Brown midrib sorghum[d]	4591	[208]
Rotated corn[d]	7737	[208]
Continuous corn[d]	7087	[208]

[a] Ethanol yields from stover components only.
[b] Ethanol yields from the average of all entries for a same species.
[c] Ethanol yields from grain, bagasse and leaves, and extracted fermentable carbohydrates combined.
[d] Ethanol yields from stover and grain components combined.

Ethiopia and Kenya, which have a relative low capital cost limited productivity. However, commercial anaerobic digestion to biogas has been developed in large-scale plants with 830 m^3 per day in 2003 and 1430 m^3 per day in 2005 in Rwanda in order to treat toilet wastes and generate biogas for cooking. Anuannom Industrial Projects Limited in Ghana has a biodiesel plant (factory costing $1.2 million with 360,000 ton production/annum) that has been under construction since 2003 with the intention of being the first commercial biodiesel plant in Africa. Balan et al. [193] studied biofuel demonstration and commercialization activity in the United States and the Europe Union. They reported that a majority of projects were either at pilot/demonstration scale or under advance stages of construction of commercial plants and bioethanol via a biochemical route that is the current leading process strategy in those areas. These biofuel conversion strategies using lignocellulosic biomass are the results of many years of innovative and collaborative efforts. Brown[194] investigated 10 constructing commercial-scare biofuel projects that employed a diversity of conversion pathways in the United States in 2013. By 2014, those biofuel facilities were expected to achieving 215 million gallons of annual production on a gasoline-equivalent basis. Among this annual output, hydrocarbon-based fuels and ethanol-based fuels were expected to account for 52% of the total with 111 million gallons and 48% of the total with 104 million gallons, respectively.

4.2. Future prospects and constraints to be overcome

Although big bluestem is a promising feedstock for bioenergy conversion, various constraints remain. Pretreatment is key and most expensive part of bio-ethanol conversion. However, current pretreatment methods still require relatively high cost, and some factors affecting conversion efficiency are not yet well understood. Most current chemical and physical pretreatment processes are limited by lack of intensity in order to release sugars in high yield or excessive intensiveness, resulting in degradation of sugars (e.g., to furfural). Therefore, efficient pretreatment processes associated with low cost must be developed in order to update traditional processes.

A further disadvantage of most traditional processes is that resulting hydrolysate streams contain a mixture of 5- and 6-carbon sugars. Commercial yeast strains cannot effectively utilize 5-carbon sugars, which account for approximately 20–25% of big bluestem. In order to save fermentation time and enhance product yield, a novel microorganism combination must improve to ferment 5- and 6-carbon sugars simultaneously. For feedstock management, reduction of land cost is a core indicator of the degree of sustainability.

Millions of acres of marginal lands have been taken out of row crop agriculture and converted to CRP lands [2]. Kansas, Nebraska, and South Dakota enrolled up to 5 million acres of CRP lands in 2010, for the purpose of restoring grasslands from marginal agricultural lands to grasslands [195]. CRP grasslands, which have been previously ignored, are now considered to be valuable resources because they could be used for low input, sustainable feedstock, thereby avoiding competition with prime farmlands [196]. In turn, perennial grasses on the 11 million ha of marginal lands could potentially produce 5.5 billion gallons of ethanol annually, contributing 25% to the target of US Energy Independence and Security Act of 2007 [197]. As one of the best candidates of perennial energy grass, big bluestem has already been planted for prairie restoration on CRP lands. Thus, if big bluestem as a bioenergy resource could be developed on marginal lands, it would produce significant amounts of biofuels and substantially avoid competition with prime farmlands [196] while maintaining ecosystem services [8] and wildlife diversity [20].

Another issue limiting wide acceptance is difficulty in planting and establishment. Seed requires processing to remove hairs and planting requires special drills. In addition, research on breeding and germplasm development should be carried out in order to identify and recommend particular accessions with suitable traits appropriate for improving biomass yield and identifying favorable biofuel conversion characterizations. Genotyping-by-sequencing (GBS), high throughput sequencing, provides opportunity to link genotype to phenotypes, including biomass, drought tolerance, and biofuel potential [198]. GBS uses enzyme-based complexity reduction coupled with DNA barcoded adapters to produce multiplex libraries of samples ready for "next generation" sequencing.

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