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Research paper

Characterization and compositional analysis of agricultural crops and residues for ethanol production in California

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ABSTRACT

This study was carried out in order to analyze characteristic and composition of crops, crop wastes, and residues including a variety of sugar beets and melons, tomato, Jose tall wheatgrass, wheat hay, and wheat straw in California. Ethanol potential was estimated from different scenarios in using carbon sources of feedstock during fermentation, including the new information of using pectin–derived galacturonic acid for ethanol production. Sugar beet appears more favorable than other feedstocks because of its high sugar content (67–75% dry basis, db) and the highest crop yield, resulting in the greatest ethanol potential of 591 m^3 Gg^{-1} db when all carbohydrates are used during fermentation, with the California area–based potential of 1273 m^3 km^{-2}. Fermentation of polygalacturonic acid can increase the ethanol potential of sugar beet leaves up to 30% over the fermentation of hexoses alone, increasing the theoretical ethanol potential to 340 m^3 Gg^{-1} and the area–based yield of 497 m^3 km^{-2}. Melons and tomato containing 42–69% by mass of soluble sugars showed ethanol potentials in a range of 448–545 m^3 Gg^{-1} db and the area–based yield of 25–53 m^3 km^{-2}. The theoretical ethanol yield from lignocellulosic feedstocks tested can be maximized up to 470–533 m^3 Gg^{-1} db and 291–300 m^3 km^{-2} when the primary components from cellulose (27–39% db) and hemicellulose (26–30% db) are utilized. The information on composition and ethanol potential is important for determining biofuel feedstock and developing technology for efficient use of bioresource.

1. Introduction

Increasing energy demand, uncertainty and instability of fossil fuel supply, and environmental concerns associated with the use of petroleum–based fuels have significantly increased the development and use of renewable energy worldwide. In the United States, fuel ethanol production increased from approximately 1.3 million cubic meters in 1982 to 57 million cubic meters in 2015 [1]. To promote biofuel production under the 2007 Energy Independence and Security Act (EISA), the Renewable Fuel Standard (RFS) mandates the production of ethanol to 136 million cubic meters by the year 2022 [2].

Nearly 95% of ethanol production in the world is from agricultural biomass [3], consisting of approximately 60% from starch crops and 40% from sugar crops. Commercial ethanol fuel is presently produced primarily from corn (*Zea mays*) in the US, China and Canada; sugarcane (*Sacchrum officinale*) in Brazil; sugar beet (*Beta vulgaris*) in France; and to a lesser extent wheat (*Triticum aestivum*) in China and Canada; and cassava (*Manihot esculenta*) in Thailand [4]. Although corn–based and sugar–based ethanol are being blended with gasoline or used as direct fuel, in 2012 the world fuel ethanol production only represents 6.5% of the motor gasoline consumption of 1.31 billion cubic meters per year worldwide [5].

Lignocellulosic biomass is the world's largest renewable resource and thus considered to be the most promising biofuel feedstock. According to the U.S. Department of Energy's (DOE) [6], in the United States the total forest and agriculture biomass are about 473 billion dry kilograms (Tg db) in 2012. Under the baseline projected consumption of currently used resources, the forest residues and wastes, the agricultural residues and wastes, and energy crops show a total of 1094 Tg db by 2030. The energy crops are those grown specifically to supply consistent quality of feedstocks for the production of biofuel and biopower [6]. Perennial grasses, trees, and some annual crops are used for energy production, for

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example, switchgrass (*Panicum virgatum*), sugarcane (*Saccharum* spp.), sorghum (*Sorghum bicolor*), and poplar (genus *Populus*). The total agricultural residues and wastes alone are about 247 Tg db in 2012 and increase to 368 Tg db by 2030. In 2022, the year in which the revised RFS mandates the use of 136 million cubic meters a year of renewable fuels, the feedstock projected under the baseline scenario shows 602 Tg db of potential resource (100 Tg db of forest biomass, 221 Tg db of crop residues, and 282 Tg db of energy crops). This potential resource is more than sufficient to provide feedstock to produce the required 76 million cubic meters of lignocellulosic biofuels mandated by the US government.

The substantial availability and relatively low cost make agricultural residues the most promising biofuel feedstock. While corn stover, corn stalks, rice and wheat straws, and sugarcane bagasse have received much attention for ethanol feedstocks as they are available in large quantities at locations close to current ethanol production facilities [7], there is limited information for other specialty crops and agricultural residues in term of structural compositions for fuel–feedstock application. California is the leading state for producing agricultural products in the nation, providing a wide variety of crop and specialty biomass. Sugar beet have been produced as a local crop in California for more than 100 years [8], and achieved the highest crop yield in the country [9]. Sugar beet leaf is an agricultural residue produced during sugar beet production, accounting for 40–50% of total crop wet weight. A great amount of sugar beet leaves remaining unused is potentially utilized as feedstock for biofuel production along with sugar beet root.

Economic feasibility of ethanol fuel production from a variety of starch and sugar crops, and grain residues was previously evaluated for the Sacramento Valley, California to estimate breakeven prices for each feedstock for a cooperative scale plant [10]. According to Meo's study (1984), fodder beet and wheat straw was the least–cost feedstock for starch and sugar, and lignocellulosic feedstocks, respectively, leading to the lowest breakeven prices for ethanol production. Wheat straw was the cheapest feedstock among residue lignocelluloses tested [10]. Sugar beet has an advantage for their cheaper storage costs, as they can be over––wintered in the ground.

Ethanol yield can be estimated theoretically from the amount of fermentable sugars and polysaccharides present in the feedstock and may be used as a general indicator of feedstock quality. In the past, soluble sugars and structural carbohydrates (cellulose and hemicellulose) have been considered to be the main precursors for ethanol production in lignocellulosic biomass. Pectin, a significant component in many types of biomass, such as beets, fruits and vegetables, is another potentially large carbon source for ethanol production.

Various microorganisms are available for producing ethanol from sugars and sugar acids derived from biomass. Wild–type *Saccharomyces cerevisiae* have been used for fermenting hexose sugars (C6). Modified strains of *S. cerevisiae* have been developed for fermentation of pentose sugars, such as xylose and arabinose [11–13]. *Escherichia coli* KO11 can ferment galacturonic acid to produce equal molar amounts of ethanol and acetate [14,15]. In addition, *Clostridium* species (*C. phytofermentans* [16,17] and *C. cellulyticum* [18]) and ethanologenic constructed bacteria in genus *Erwinia* (*E. chrysanthemi* EC16 and *E. carotovora* SR38 [19]) showed potential for the direct hydrolysis and fermentation of pectin to ethanol.

To determine which herbaceous crops are the most feasible for use as biofuel feedstock in the future, it is important to examine biomass yield and availability, biomass characteristics and composition, and potential ethanol yield. Much work has been reported in the literature on feedstock characterization for agricultural crops and residues. However, there is a lack of complete analysis in biomass composition intended for biorefinery feedstock. In addition, most studies focus on crude protein and fiber content. In order to design efficient conversion processes and conditions, it is important to know the primary components of biomass, such as cellulose, hemicellulose, pectin and lignin and understand their contribution to the resulting biofuels.

This study was conducted as part of a research and demonstration project that is aimed to develop a biorefinery plant in the Central Valley of California for producing ethanol as biofuel from sugar beets, waste fruits and vegetables, grasses, and crop residues. The objectives of this study were to analyze the physical characteristics and chemical composition of the selected biomass, and evaluate and compare their estimated ethanol yield potential on a mass and area basis.

2. Materials and methods

2.1. Biomass feedstock preparation

Fifteen biomass samples were collected and analyzed. The selected samples included sugar beet roots and leaves, from EGC183, ECG184, ENC115 and B4430R varieties, cantaloupe, honeydew, watermelon, Roma tomato, Jose tall wheatgrass, wheat hay (with grain) and wheat straw (without grain). Melons and tomato are those fruits discarded by the growers or processors due to poor quality. Samples of melons, Jose tall wheatgrass, wheat hay and wheat straw were provided by local farmers and collaborators. Sugar beet B4430R variety was received from U.S. Agricultural Research Station in Salinas, California. Three sugar beet varieties (EGC183, ECG184, ENC115) provided by KWS (Betaseed, Inc.) have been grown at UC Davis field plots, and small samples have been harvested for storage.

Herbaceous crop samples (sugar beet, melons and tomato) were collected and ground using an industrial food chopper (Hobart, USA) followed by a food processor (Cuisinart, USA), and stored at −20 °C. The feedstock samples were dried using a freeze–drier (VirTis Gardiner, NY) and milled with a small 40–mesh Wiley knife mill (Thomas Scientific, USA). For grasses (wheatgrass, wheat hay and wheat straw), naturally dried samples were directly milled using a hammer mill (Fritsch, Germany) followed by a small 40–mesh Wiley knife mill (Thomas Scientific, USA). The fresh and dried samples were analyzed for moisture (MC), total solids (TS), and volatile solids (VS) contents. The dried ground samples were used for analyses of chemical composition and nutrients.

2.2. Physical property analysis of biomass

Biomass feedstock samples were analyzed for moisture (MC), total solids (TS), volatile solids (VS), and ash contents by the constant weight method through drying at 378 K. Total ash was determined as residual solids after calcination at 823 K. These analyses were conducted by using the standard methods described in *Standard Methods for the Examination of Water and Waste Water* by American Public Health Association [20]. Each sample was analyzed in triplicate.

2.3. Chemical compositional analysis of feedstock

Compositional analyses were performed by the UC analytical laboratory using the methods of acid and neutral detergent fibers. Cellulose and lignin were determined by the AOAC method [21] using a hot, acidified detergent solution to dissolve cell solubles, hemicellulose, and soluble minerals, leaving a residue of cellulose,