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Municipal solid waste as a suitable substrate for butanol production as an advanced biofuel

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ABSTRACT

The biodegradable fraction of municipal solid waste (BMSW), dominantly composed of starchy and lignocellulosic materials, has high potential to be used for liquid biofuel production. Hot water or dilute acid treatment at high temperature was utilized for the solubilization or hydrolysis of the starch fraction and pretreatment of the lignocellulosic fraction. The treatment liquor, which was rich in sugars and starch, was evaluated for acetone, butanol, and ethanol (ABE) production by *Clostridium acetobutylicum*, and it was found that phenolic compounds, especially tannins, critically inhibited the butanol production. To improve ABE production, the extraction of phenolic compounds prior to hot water or dilute acid treatment was evaluated. Among the evaluated extractants, i.e., acetone, ethanol, butanol, and water, ethanol showed the highest amount of tannin extraction, resulting in an 87% reduction in tannin content. Dilute acid treatment of the ethanol extracted BMSW at 140 °C for 60 min resulted in a liquor containing 23 g/L glucose and 41 g/L soluble starch, which was fermented to the highest ABE concentration of 17 g/L with productivity of 0.24 g/L/h. The fermentation of liquor obtained by dilute acid treatment of butanol, acetone, and water-extracted BMSW was accompanied by 9, 6, and 4 g/L ABE production. Even by hot water treatment, the liquor obtained from ethanol extracted BMSW was fermented to the highest ABE concentration of 8 g/L. In addition to the liquor, the pretreated lignocellulosic material was subjected to enzymatic hydrolysis and ABE fermentation, leading to production of 5–6 g/L ABE. This process resulted in the production of 83.9 g butanol, 36.6 g acetone, and 20.8 g ethanol from each kg of BMSW. Moreover, the co-production of ethanol by ABE fermentation reduced concerns about organic extractor loss in the extraction process, which was inescapable in the tannin extraction process.

1. Introduction

Municipal solid waste (MSW) includes a wide range of materials, including metals, plastics, paper, wood, food, and other waste. Kitchen and garden waste are two major biodegradable components of MSW. The US Environmental Protection Agency reported that 258 million tons of MSW was generated in the United State in 2014, which was a 7% increase compared to that of 2000 [1]. In five step directive for municipal solid management, at first step it was preferred to prevent waste production. Then, reuse and recycle were second and third priority, respectively. Recovery including energy recovery (mostly by incineration) and landfilling were the least desirable steps in municipal solid management [2].

Landfilling [3], combustion [4], and composting [5] are three major practices of MSW management worldwide. Among these alternatives, landfill is the most widely used process, accounting for management of over 50% of total generated MSW in 2014, worldwide [6]. However, it causes many problems to modern society because of increased waste generation, driven by population growth, and decreasing availability of landfill space [7].

According to the Iranian Department of Environment (DOE), in 2013, nearly 20 million tons of MSW was produced annually in Iran, among which 20% were generated by villagers, while urbanites produced the remaining 80%, and only 20% was recycled. The main process for the management of MSW in Iran is currently landfilling; about 15 million tons of MSW with more than 70% biodegradable fraction were landfilled annually [8].

Inevitable production of MSW in huge amounts with such a high biodegradable fraction provides high potential for its bioconversion to value-added products, e.g., biofuels. Utilization of the biodegradable

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fraction of municipal solid waste (BMSW) as an available feedstock at zero or negative cost may improve the economic status of biofuel production and help it become an attractive alternative for MSW management. The production of a variety of bioproducts, e.g., lipids [9], organic acids [10], biogas [11–13], and bioethanol [14], from BMSW has been reported. Although, in all thermal and biochemical conversion process some inert BMSW residue was remained that had to be landfilled. After biochemical and thermal processes the amount of BMSW was significantly lower than initial mount. So, landfilling is the terminate step in municipal solid management procedure [15].

The major practice for the management of biodegradable materials in MSW are currently anaerobic digestion in landfill, mainly without gas collection [16–22]; however, despite facing a number of challenges, the production of liquid biofuel from the waste is highly important to fulfill the energy needs of the transportation sector.

Recently, acetone-butanol-ethanol (ABE) has attracted great attention as an advanced biofuel, addressing some challenges in liquid biofuels, due to its superior properties compared to ethanol, including higher energy density, blending with gasoline at high concentrations, hydrophobic nature, and its lower volatility [23–25]. Biobutanol was also reported as a promising candidate for blending with diesel [26] and gasoline/Jet A [27] fuels. Along with the inherent environmental advantages of using renewable biofuels, decreasing exhaust gas temperature and NOx emissions are benefits of butanol/diesel blends. However, the relatively high cost of substrate is one of the most important obstacles in commercial scale production of butanol from sugar- and starch-based materials [28].

Lignocellulosic biomass was suggested as the substrate for cost-effective production of ABE, due to its availability and low price [29,30]. A number of studies have been conducted on producing ABE from different lignocelluloses, including rice straw [31], agricultural waste [32], woody biomass [33], wheat straw [34], corn stover [35], and barley straw [36]. Lignocelluloses are not fermentable by the solvent-producing *Clostridia*; thus, a suitable pretreatment and hydrolysis stages are necessary for converting lignocelluloses to fermentable hydrolysates [30]. Furthermore, low-cost starchy substrates, e.g., waste starch and sorghum grains, were also suggested for biobutanol production, where starch is directly utilized in fermentation by *Clostridia* as a result of its relatively high extracellular amylolytic activity. Similar utilization of MSW, mostly in the form of lignocellulosic and starchy wastes, for biobutanol production may change MSW from a threat to an opportunity. However, to our knowledge, MSW has not been evaluated for biobutanol production.

In this study, the biodegradable fraction of MSW was evaluated as a substrate for biobutanol production. Through hot water or dilute acid treatment at 140 °C for 60 min, the starch fraction of BMSW was solubilized/hydrolyzed into its liquid phase, leaving beside a pretreated lignocellulosic solid. The liquor, rich in soluble starch and sugars, as well as the hydrolysate obtained after enzymatic hydrolysis of the pretreated solid, was subjected to fermentation by *Clostridium acetobutylicum*. The effects of inhibitors released from MSW on ABE production were investigated. Extraction of inhibitors from BMSW into a solvent prior to hot water or dilute acid treatment was used for the improvement of ABE production from starchy liquor and lignocellulosic solid. In addition to water, the organic solvents of acetone, butanol, and ethanol were evaluated as recyclable extractants, whose loss can be compensated by a portion of ABE produced through ABE fermentation.

2. Materials and methods

2.1. Raw materials

Municipal solid waste used in this study was collected from the urban waste compost plant located in the Gardaneh Zeynal region, Isfahan, Iran. The plant, with a total land area of 100 has, is used for collecting all MSW of the Isfahan city, with nearly 1200 tons per day capacity. In the collection site, inorganic fractions of MSW (around 36%), including metals, plastics, and glasses, were separated by passing over a hammer mill, magnet separator, and drum sieve as well as manual selection. MSW is pushed to the conveyors by a large front-end loader, where a hammer mill equipped with double anti-explosives rotors breaks up large pieces. The milled MSW passes over magnets, where metals are separated from the waste stream. Drum sieves (50-mm mesh size) is used to screen into different size classes for further screening on vibrating conveyors. Recyclable materials, including paper, cardboard, and newspaper, were separated for reusing. The remaining organic fraction, i.e., starchy materials, kitchen, and garden waste, was considered as the biodegradable fraction of municipal solid waste (BMSW), and used in this study. The mass fraction of different ingredients of BMSW was analyzed (Table 1). A sample of the BMSW collected in autumn 2016 was air dried, hammer milled, and sieved by 20 and 80 mesh to achieve sizes between 833 and 177 μm. The milled BMSW was stored in plastic bag at 4 °C for further use.

Table 1
The composition of the biodegradable fraction of municipal solid waste (BMSW).

Component	Unit	BMSW
Starch-based materials	%w/w	58.56 ± 0.40
Lignocellulosic components	%w/w	20 ± 0.32
Lipids	%w/w	6.5 ± 0.030
Proteins	%w/w	8.21 ± 0.21
Pectins	%w/w	10.13 ± 0.80
Water extractives	%w/w	20.26 ± 0.02
Ethanol extractives	%w/w	12.07 ± 0.21
Total solids (TS)	%w/w	92.40 ± 0.70
Volatile solids (VS)	%w/w	85.72 ± 0.57
Total phenolic component	Equivalent mM gallic acid/g MSW	0.36 ± 0.21
Tannins	Equivalent mM gallic acid/g MSW	0.20 ± 0.15

2.2. Pretreatment

The hot water and dilute acid treatment were carried out by soaking 21.7 g of BMSW in 195.3 g distilled water or dilute sulfuric acid solution (0.5% W/W) in a high pressure stainless steel reactor with 500 mL working volume [37,38]. The treatment of BMSW was conducted at a solid:liquid ratio of 1:10 (w/w) (based on total solid). The reactor was placed in an oil bath, equipped with a temperature controller (One 10, Memmert, Germany), and heated at the rate of 3 °C/min until reaching the desired temperature of 140 °C. Reactor temperature and pressure were identified by the temperature indicator and pressure gauge, respectively, on the reactor. After the desired duration of 60 min, the reactor was cooled down in an ice bath. The pretreated materials were then separated and washed with fresh water until neutral pH. The pretreated materials were freeze dried, weighed to calculate the solid recovery, and stored at 4 °C until further use. In addition, the liquid fraction was stored at −18 °C. Moreover, to evaluate the potential of ABE production from the starch and lignocellulose fraction of untreated BMSW, the starch fraction of BMSW was separated by dissolving in water at 90 °C. The results obtained through the fermentation of dissolved starch and the hydrolysate of untreated solid were used as control.

2.3. Enzymatic hydrolysis

The untreated and pretreated BMSW samples were hydrolyzed by using cellulase (Cellic® CTec2) and hemicellulose (HTec2) enzymes complex with a ratio of 9:1 with cellulase activity of 20 filter paper unit (FPU) per g dry weight of substrate. The enzymes were kindly provided by Novozymes (Bagsvaerd, Denmark) for this study. An amount of 1.5 g of untreated and pretreated material was added to 30 mL sodium citrate buffer (50 mM, pH 4.8). The suspension was autoclaved at 121 °C for 20 min. After addition of enzymes, the hydrolysis was conducted at