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Efficient conversion of municipal solid waste to biofuel by simultaneous dilute-acid hydrolysis of starch and pretreatment of lignocelluloses

Peyman Mahmoodi[a], Keikhosro Karimi[a,b,*], Mohammad J. Taherzadeh[c]

[a] Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Industrial Biotechnology Group, Research Institute for Biotechnology and Bioengineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[c] Swedish Centre for Resource Recovery, University of Borås, 50190 Borås, Sweden

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ABSTRACT

The organic fraction of municipal solid waste (OFMSW) is a complex mixture of easily digestible compounds, mainly starchy materials, and hardly digestible compounds, mainly lignocelluloses. Thus, OFMSW has a high potential for biofuel production after the hydrolysis of carbohydrates. In this study, dilute-acid treatment was used for the hydrolysis of starchy materials, eliminating the amylases enzymes requirement. Besides, the acid treatment acted as a pretreatment for the improvement of lignocelluloses fractions prior to the enzymatic hydrolysis of lignocelluloses. The acid treatment was conducted with 0.5 and 1% (w/w) sulfuric acid at 130 and 160 °C for 0, 30, and 60 min. The treatment with 1% acid at 130 °C for 60 min resulted in the hydrolysate with the highest glucose concentration of 43.2 g/L, mainly originated from starchy materials, and the subsequent enzymatic hydrolysis of the treated solids resulted in a hydrolysate containing 23.4 g/L glucose, mainly from cellulose. These hydrolysates, containing different sugars and inhibitors, were then subjected to ethanolic fermentation using a highly inhibitor-tolerant strain of Zygomycetes fungi, *Mucor indicus*. Using acid treatment with 1% at 130 °C for 60 min, without detoxification, the ethanol yield of 44.6 and 44.4 g per 100 g glucose was obtained from hydrolysate and acid treatment liquor, respectively. The liquid remained after the separation of ethanol from fermentation liquor and the residual solid remained after enzymatic hydrolysis were subjected to anaerobic digestion for biogas production. Overall, 194.0 g ethanol and 144.8 L methane were produced from each kg of dry OFMSW through the consecutive processes. Therefore, without detoxification and amylases requirement, all biodegradable parts of MSW were converted to bioenergy in the form of ethanol and biogas, resulting in the production of 10,453 kJ energy and 326.6 mL gasoline equivalent from each kg of dry OFMSW.

1. Introduction

Production of MSW is a threat to environment worldwide. Proportional to population growth, the amount of MSW generation (522–759 kg per person per year) is increasing and nowadays more than 2 billion tons MSW per year is produced worldwide [1–3]. The organic fraction of municipal solid waste (OFMSW) has a high potential for the production of biofuels because of availability in huge amounts, negative price, and the existence of biodegradable materials (e.g., lignocelluloses, starch, lipid, pectin, and protein) [4–6]. Most of biodegradable components available in MSW could be digested and converted to biofuels, e.g., ethanol and biogas. Production of biogas from OFMSW is already in the market [7–10]. Different biodegradable fraction of MSW, e.g., carbohydrates, lipids, and proteins, can be converted into biogas after a 4-stage process, comprising hydrolysis, acidogenesis, acetogenesis, and methanogenesis [11,12].

Ethanol is the most favorable liquid biofuel, which can be produced from the biodegradable fraction of MSW. Food and household wastes [13,14], two major parts of MSW, was used for ethanol production with a yield of 25 g/L ethanol per 100 g/L food residues using *Saccharomyces cerevisiae* [14]. Corrugated cardboard, another component of MSW, was also used for ethanol production after dilute-acid prehydrolysis and enzymatic hydrolysis [15].

As lignocelluloses are a dominant part of MSW and due to their recalcitrant structure, a pretreatment is necessary to improve the production of ethanol and biogas from MSW [16,17]. Pretreatment is known to be the crucial process to prepare the lignocelluloses for enzymatic hydrolysis and fermentation [18]. The main goals of pretreatment are lignin and hemicellulose removal, reduction of cellulose crystallinity, and increase in the accessible surface area for hydrolytic enzymes [16]. Pretreatment methods are usually categorized into physical, physic-chemical, chemical, biological, and their combination

* Corresponding author at: Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran.
E-mail address: karimi@cc.iut.ac.ir (K. Karimi).

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[19]. Acid pretreatment processes are comprised of two categories, i.e., treatment at low temperature with high acid concentration and treatment at high temperature with low acid concentration [16]. Dilute-acid pretreatment is among the most successful methods for the improvement of biofuel production from lignocelluloses [16,20]. However, different inhibitors, including hydroxymethylfurfural (HMF), furfural, and phenolic component are produced during acid treatment [16]. These components have an inhibitory effect on microbial growth, cell membrane function, and glycolysis in most ethanol producing microorganisms [21]. Among the ethanol producing microorganisms, Zygomycetes fungi, particularly *Mucor indicus*, are found to be among the most resistant microorganisms to the inhibitors [22].

This study was aimed at efficient production of ethanol from OFMSW and biogas from the residues. Dilute-acid treatment at different conditions was evaluated for the hydrolysis of starchy materials and pretreatment of lignocelluloses fractions of OFMSW for ethanol production. Thus, dilute-acid treatment was used to eliminate the need for the enzymatic hydrolysis of starchy materials; however, the cellulosic part was enzymatically hydrolyzed. The hydrolysates were then fermented by *Mucor indicus*. Subsequently, the residual solid from enzymatic hydrolysis and liquid from fermentation broth (after ethanol separation) were subjected to anaerobic digestion for biogas production.

2. Materials and methods

2.1. Raw material

Municipal solid waste was collected in summertime from Isfahan MSW landfill site (Isfahan, Iran). This MSW was composed of different materials. The inorganic materials, e.g., glass, metal, and plastic and the recyclable materials, e.g., paper, cardboard, and newspaper, were separated from MSW. The organic fraction of MSW (OFMSW) was dried, milled, and sieved for achieving a size of between 833 μm (20 mesh) and 177 μm (80 mesh). Then, it was stored at room temperature in sealable plastic bags.

2.2. Acid treatment

The treatment of OFMSW with 0.5% and 1% (w/w) sulfuric acid was conducted at two temperatures (130 and 160 °C) and three reaction times (0, 30, and 60 min) at a solid:liquid ratio of 1:10 (w/w) (based on total solid) in a 500 mL stainless steel high-pressure reactor (101SSHPR, Steel Sanat, Isfahan, Iran). The reactor was heated at a rate of 7 °C/min in an oil bath and the reaction time was considered when the reactor reached the desired temperature.

In the pretreatment for 0 min, the reactor was heated to the desired temperature, and then the reactor was immediately cooled. After acid treatment, the reactor was cooled in an ice water bath, and the residual solid was separated from the liquid phase by filtration. The solid residue was washed with distilled water to achieve neutral pH. Then, the solid residue was dried for 24 h in a freeze-dryer (Christ, alpha 1–2 LD model, Germany). The treatment liquor, i.e., the liquid fraction of dilute-acid treatment, was stored at 4 °C until ethanolic fermentation.

2.3. Cellulose hydrolysis

Two commercial enzymes of Cellic® CTec2 and HTec2 (kindly provided by Novozymes A/S, Denmark) in a 9:1 ratio, were used for enzymatic hydrolysis of lignocellulosic carbohydrates. The cellulase activity of the enzyme mixture was 95 filter paper units (FPU) per ml, measured using the standard method presented by Adney and Baker [23].

The untreated and dilute-acid treated OFMSW were hydrolyzed using 20 FPU per gram of dry substrate. The hydrolysis was carried out at the initial substrate concentration of 50 g/L (based on dry weight) in 0.05 M sodium citrate buffer at pH 4.8. To do this, 2 g substrate was added to 40 mL sodium citrate buffer in 118 mL sealable glass bottle and autoclaved at 121 °C for 20 min. The enzymatic hydrolysis was carried out in a shaker incubator at 45 °C and 120 rpm for 72 h. After hydrolysis, the cellulosic hydrolysate was separated from the residual solid substrates by centrifugation at 4000 rpm for 10 min and stored at 4 °C until ethanolic fermentation.

2.4. Ethanol production

The fungus *Mucor indicus* CCUG 22,424 (Culture Collection University of Goteborg, Sweden) was used for ethanolic fermentation. The fungus was cultivated on agar slants at pH 5.5, prepared with (g/L): peptone, 10; glucose monohydrate, 40; and agar, 20. The slants were incubated at 32 °C for 5 days and then stored at 4 °C [24].

M. indicus biomass for fermentation was prepared in 118-mL sealable glass bottle with 50 mL medium containing (g/L): yeast extract, 5; $(NH_4)_2SO_4$, 7.5; KH_2PO_4, 3.5; $MgSO_4{\cdot}7H_2O$, 0.75; $CaCl_2{\cdot}2H_2O$, 1; and glucose, 50, at pH 5.5 ± 0.1 [24]. The bottles were sterilized in an autoclave at 121 °C for 20 min. Next, a slant of the fungus was dissolved in 10 mL of sterile distilled water to obtain spore suspension. Then, 5 mL of this spore solution that included 5–6 × 10^6 spores/mL was added to each bottle. The bottles were purged with pure nitrogen gas for 5 min and then incubated at 32 °C and 150 rpm for 30 h..

For ethanol production, 20 mL of hydrolysates was supplemented with 2 g/L yeast extract, 2 g/L $(NH_4)_2SO_4$, 0.25 g/L $MgSO_4{\cdot}7H_2O$, 4 g/L KH_2PO_4, and 2 g/L NH_4PO_4 in 118-mL sealable glass bottles. The bottles were autoclaved at 121 °C for 20 min. Next, 0.02 ± 0.001 g of biomass (based on dry weight) was added to each bottle. The bottles were purged with pure nitrogen gas for 5 min and incubated at 37 °C and 150 rpm for 72 h. All ethanolic fermentation experiments were performed with two replicates.

2.5. Biogas production

The inoculum for biogas production was obtained from a 7000-m^3 mesophilic anaerobic digester (Isfahan Municipal Wastewater Treatment, Isfahan, Iran). The inoculum was stabilized for 5 days at 37 °C.

Ethanol was separated by distillation from the ethanolic fermentation process, and the remaining mixture together with the residual solid remained after enzymatic hydrolysis were subjected to anaerobic digestion for biogas production. The process was conducted according to the method presented by Hansen et al. [25] in 118-mL sealable dark glass bottles. In each bioreactor, 0.25 g substrate (based on volatile solids, VS) was mixed with 20 mL inoculum and 5 mL deionized water. A blank experiment containing inoculum and deionized water was prepared to determine the inoculum's methane production. Besides, a glucose sample was run for comparison purpose. To create anaerobic conditions, the reactors were purged with nitrogen gas for 5 min. Then, the reactors were incubated at 37 °C for 50 days. The produced biogas was analyzed for methane and carbon dioxide contents every 3 days during the first 15 days and then every 5 days until 50 days.

All anaerobic digestions were carried out in triplicates.

2.6. Analytical methods

All samples analyzed for structural carbohydrates, lignin, and ash contents according to the standard method presented by Sluiter et al. [26]. Starch concentration in the dilute-acid liquor was measured based on enzymatic hydrolysis using α-amylase (Liquezyme, Novozymes A/S, Denmark) and glucoamylase (Dextrozyme GA, Novozymes A/S, Denmark) enzymes to the liquid of acid treatment. The difference between glucose concentration after and before enzymatic hydrolysis showed the concentration of starch in the liquid by the following equation [27]: