Bioethanol and biogas production from an alternative valorisation pathway for green waste

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Introduction

Green waste (GW) includes mostly leaves, branches and lignocellulosic debris from grass clippings, hedge cuttings and tree prunings. The amount of this type of biomass continues to increase with the expansion of urban and green space areas. Green waste for energy production has been suggested to be more environmentally friendly However, their chemical composition is complex and varies seasonally and locally. Just a few studies have been carried out on estimating the potential of green waste towards biofuel production. It has been estimated biofuel produced from green waste can offset 1.6–6.5% of the city's transport gasoline demand in Singapore (Shi *et al*, 2013). The potential and feasibility of using green waste biomass for bioethanol and biogas production shall be explored further within this study.

Materials and Methods

Raw materials: Milled green waste utilized in the present study was provided by the Municipality of Zografou, Attica, Greece. It was transferred to the Unit of Environmental Science and Technology (UEST), School of Chemical Engineering, National Technical University of Athens.

Green waste had the following composition (%w/w dry base): Volatile solids 95.50 ± 1.77, water soluble solids 17.73 ± 1.03, cellulose 33.48 ± 2.44, hemicellulose 14.83 ± 4.78, acid soluble lignin 0.23 ± 0.01, acid insoluble lignin 22.28 ± 0.27.

Physicochemical Characterisation: Cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, ash and moisture were measured following the analytical procedures of NREL laboratory analytical protocols (Sluiter et al, 2012). Volatile fatty acids (VFA) were quantified by the Spectroquant Volatile Organic Acids Test kit (Merck Millipore). Ethanol, Glucose, Acetic Acid, Xylose were measured using high-performance liquid chromatography (HPLC) (0.6 mL/min, H2SO4 0.005M, H+ Column).

Chemical pretreatment: Two pretreatment schemes were applied with either dilute alkaline or dilute acid media. In the first pretreatment scheme, 20 g GW were pretreated in 0.3M dilute NaOH at 50 °C for 96 h while in the second, 20 g GW were pretreated in 0.2M H_2SO_4 at 120°C for 1 h. All experimental trials were performed thrice and the average values are presented.

Enzymatic Hydrolysis: Enzymatic hydrolysis was performed in 250 mL autoclavable bottles. NaOH or H_2SO_4 solution was used to correct the pH to the optimum pH range of 5.0-5.5. Enzymatic saccharification was performed at 50°C by the addition of a cellulolytic formulation; Cellic CTec2 (Novozymes, Denmark) for 96h with dosages of 25 and 75 μL enzyme/g cellulose. The saccharification efficiency was quantified in terms of saccharification yield, S_G as follows (Equation 1):

$$S_G = \frac{[Glucose\ produced](g\ L^{-1})}{[Theoretical\ glucose](g\ L^{-1})} \cdot 100\ \% \qquad \text{Equation 1}$$

Alcoholic Fermentation: Bioconversion of the glucose produced to bioethanol via ethanolic fermentation was achieved by the addition of Saccharomyces cerevisiae (2% w/w) in the same autoclavable bottles, at 35°C for 24h. After the 24-hour fermentation period, the solid and liquid phases were separated by centrifugation (3500rpm for 10min) and were physicochemically characterized. The ethanolic fermentation efficiency was quantified in terms of ethanol yield, Y_{eth}, as (Equation 2):

$$Y_{eth}(\%) = \frac{[Ethanol\ produced]\ (g\ L^{-1})}{[Theoretical\ ethanol]\ (g\ L^{-1})} * 100\% \qquad \text{Equation 2}$$

The glucose conversion efficiency is quantified as (Equation 3):

$$Y_{G-eth}(\%) = \frac{[Ethanol\ produced]\ (g\ L^{-1})}{[Glucose\ produced](g\ L^{-1}) * 0.51} * 100\% \qquad \text{Equation 3}$$

Anaerobic Digestion: In line with Angelidaki et al. (2009), biomethane potential tests (BMP) were executed in 250 mL autoclavable bottles aiming to assess the anaerobic digestibility of the raw and stillage GW.

Results

The VFA and TOC concentrations of the liquid phase after the acid and alkaline pretreatments of green waste are presented in Figure 1.

The production of phenolic compounds during pretreatment was relatively low for both media (136-173mg/L), indicating that phenolic compounds could not stand as an inhibitory factor for the downstream biological processes. On the other hand, the concentration of VFA was quite high for both cases, although it was almost double after alkaline pretreatment (over 14g/L), revealing possible inhibition in the enzymatic saccharification and fermentation steps.

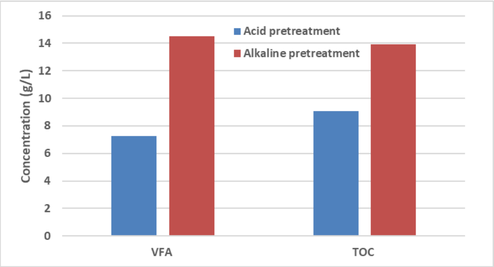
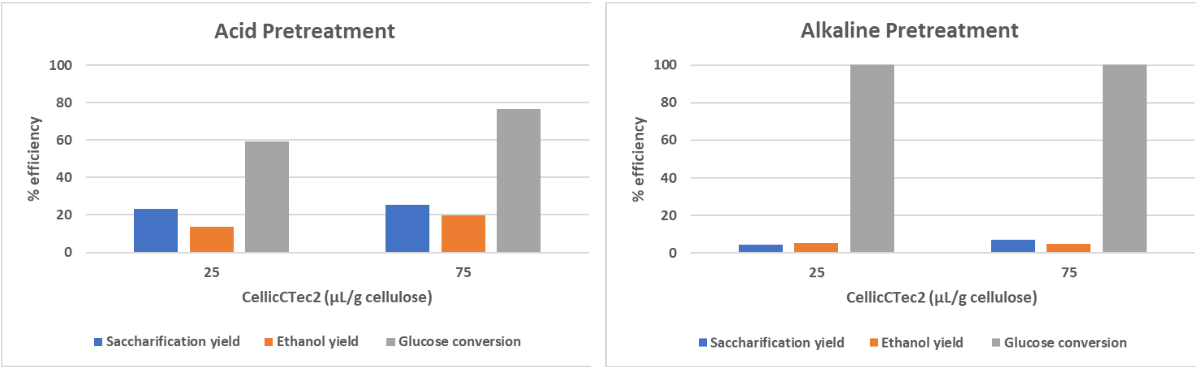


Figure 1. The production of VFA and TOC after acid and alkaline pretreatment

The saccharification yield, ethanol yield and glucose conversion efficiency are presented in Figure 2.



(a) (b)

Figure 2. Saccharification yield, ethanol yield and glucose conversion after acid (a) and alkaline (b) pretreatments

It is evident that acid pretreatment resulted in higher saccharification (23-26%) and ethanol yields (13-21%), although moderate. It is worth mentioning that after alkaline pretreatment, the glucose conversion was high implying that the fermentation step was not inhibited and the controlling process step was the saccharification.

Biogas potentials regarding the raw green waste along with the stillages GW that derived from the optimum experimental conditions for acid (0.2M H_2SO_4, 75μL CellicCtec2/g cellulose) and alkaline (0.3M NaOH, 25μL CellicCtec2/g cellulose) pretreatments were found equal to 102.4 mL biogas/g substrate, 29.02 mL biogas/g substrate and 267.09 mL biogas/g substrate respectively. It can be concluded that alkaline pretreatment promotes anaerobic digestibility of the substrate while acid pretreatment enhances the ethanol yield.

Conclusions

Green waste as an abundant but recalcitrant lignocellulosic waste stream should be suitably pretreated in order to reach its full valorisation potential. A combination of chemical pretreatment with enzymatic hydrolysis could promote different bioenergy pathways; biogas and bioethanol.

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