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Effects of thermal-HCl pretreatment process on biogas production from greenhouse residues No.IWA-503590

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INTRODUCTION

A continuous increase in the amount of organic and lignocellulosic residues makes pretreatment processes more essential before anaerobic digestion (AD). A variety of physical (comminution, hydrothermolysis), chemical (acid, alkali, solvents, ozone), physico-chemical (steam explosion, ammonia fiber explosion) and biological pretreatment techniques have been developed to improve the accessibility of enzymes to cellulosic fibers [1]. Among these, the application of chemical pretreatment methods found to be more convenient. Different kinds of chemicals applied on many lignocellulosic materials for biogas production. In this perspective, acid pretreatment involves the use of sulfuric, nitric, or hydrochloric acids to solubilize hemicellulose components and expose cellulose for enzymatic digestion [2].

The conventional disposal methods of greenhouse residues (GHR) such as unconfined storage in road edges, landfilling and uncontrolled burning causes significant environmental problems in Antalya-Turkey. Wastes disposed from greenhouses (GH) are renewable and cost free lignocellulosic residues, lacking of alternative uses, whose management is necessary to prevent environmental pollution and gain alternative utilization as a fuel biogas [3].

Even though thermal - HCl pretreatment has been applied to different kinds of lignocellulosic biomass [4-8] to enhance biogas production, there is no work investigating thermal-HCl pretreatment with the combination of biogas production from GHR in literature. Since no research has been conducted in literature to optimize the process conditions of thermal-HCl pretreatment for biogas production from GHR, main objective of this study is to investigate the optimization of thermal-HCl pretreatment process for enhancement of biogas production from GHR.

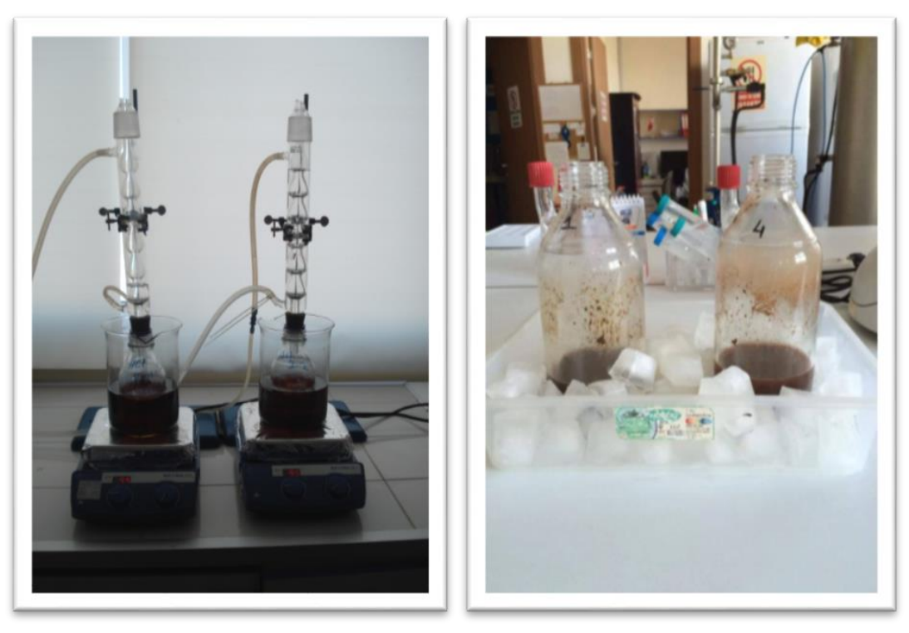
METHODS

Raw Material, Inoculum and Characterization Analyses

GHR used in this study were supplied by local growers of Kumluca–Antalya, Turkey. GHR primarily consisted of roots, stalks, leaves and fruits from tomato, pepper, cucumber, eggplant and courgette cultivation were freeze-dried and grounded to an average of 1 mm particle size for the composition analyses.

The analyses of dry matter (TS), organic matter (VS) and total chemical oxygen demand (COD) were performed according to standard methods 2540 C and 5220 B, respectively [9]. The contents of lignin, cellulose, hemicellulose and soluble matter were determined using procedures proposed by Van Soest [10]. Carbohydrate concentration and reducing sugar concentration were determined by Anthrone method [11] and DNS method [12], respectively. Protein concentration was determined by using the Lowry method [13]. Extractive matter including lipids of the GHR was determined by soxhlet extraction [14]. Elemental analyses of the GHR were performed by the CHNS elemental analyzer (LECO, CHNS-932).

Thermal-HCl Pretreatment Experiments and Optimization Process



Thermal-HCl pretreatment experiments were conducted in a 1 L laboratory scale glass reactor immersed in an oil heating bath equipped with a reflux condenser. All pretreatment experiments were performed in duplicates.

Central Composite Design (CCD) was used to illustrate the nature of the response surface in the selected experimental region and elucidate the optimal conditions of the most significant variables in the thermal-HCl pretreatment.

Variables	Low Level (-1)	High Level (+1)
Reaction Temperature (˚ C)	60	100
HCl Concentration (%)	0	5
Initial Solid Loading (%)	1	5
mixing speed	0	500

Responses
Soluble Chemical Oxygen Demand (sCOD),
Soluble Reducing Sugar (sRedSugar)
Biochemical Methane Potential (BMP)

Methane productions from raw and pretreated GHR samples were carried out by batch BMP test in mesophilic (35°C) conditions according to Carrere et al. [15]. The volume of biogas was measured by water displacement device and its composition was determined using gas chromatography (GC, Varian 4900) equipped with a thermal conductivity detector (TCD) and PPQ column.

Design expert (Stat – Ease Inc.) was used for CCD and statistical analysis of the experimental data. Developed regression model were evaluated by analysing the values of regression coefficients, analysis of variance (ANOVA), p- and F- values. The quality of the fit of polynomial models was expressed by the coefficient of determination (R^2) and adjusted determination of coefficient (Adj-R^2).

SEM was utilized to evaluate microstructural changes and to characterize the effect of thermal-HCl pretreated and raw GHR residues.

RESULTS AND DISCUSSION

Characterization of Raw GHR

Component	Unit	Value
TS	gTS/kg dry sample	913.93
VS	gVS/kg dry sample	694.09
Van Soest Fractionation		
Cellulose	%	33.12
Hemicellulose	%	23.74
Lignin	%	9.32
Soluble Matter	%	33.82
Elemental analysis		
C	%	34.16
H	%	5.03
N	%	2.39
S	%	0.82
Biochemical Methane Potential	$mLCH_4/gVS$	217

Cellulose, hemicellulose and lignin content are in the comparable range with the reported values for herbaceous agricultural residues [16]. Elemental analysis results were consistent with the previously reported compositions for the lignocellulosic materials [17].

Optimization of Thermal HCl Pretreatment Conditions for BMP

ANOVA was conducted to test the significance of the fit of the second order polynomial equations for the sCOD concentration, sRedSugar concentration and BMP. Quadratic regression models for sCOD and sRedSugar concentrations and BMP was highly significant, as it is evident from the Fisher's F-test with very low probability value (P model>F=0.0001). R^2 and Adj-R^2 were obtained as 0.8923 and 0.8321 for BMP model with the acceptable correlation. HCl concentration and mixing speed were significant for BMP model, whereas reaction temperature and initial solid loading was not a significant model term for BMP (Figure 1).

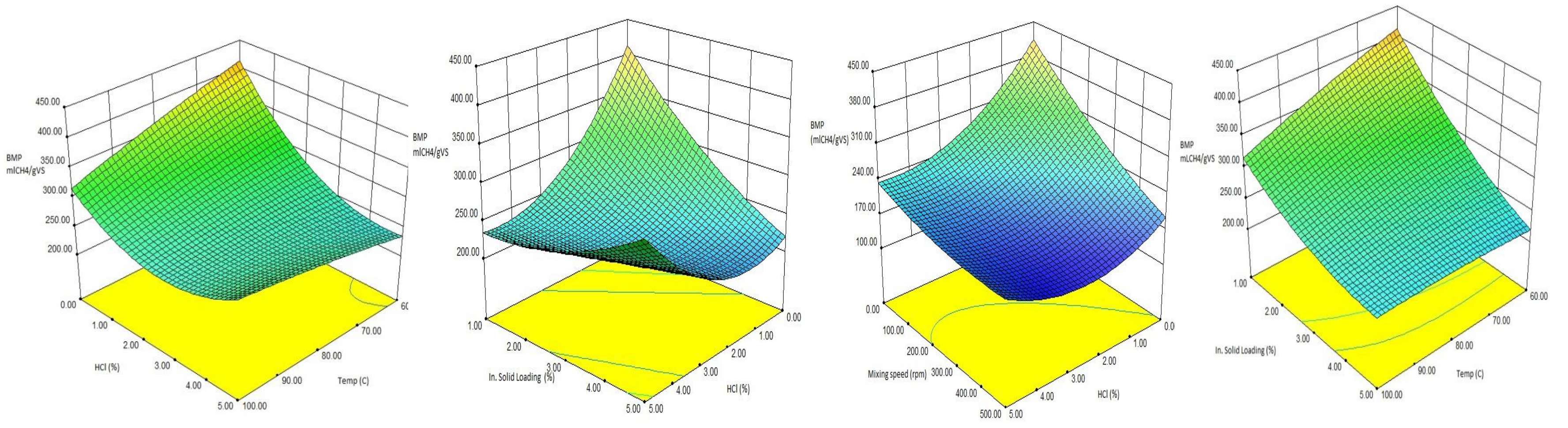


Figure 1. Effects of thermal – HCl pretreatment on biogas production

The experimental outcomes were optimized by Design-Expert® software using the approximating function of BMP. A cost driven approach was preferred in the optimization. Initial solid loading and BMP were maximized, whereas reaction temperature and acid concentration were minimized from the perspective of environmentally sustainable approach and process cost. Mixing speed, sCOD and sRedSugar concentration were set within range.

Optimum conditions were obtained with the desirability of 0.792 at 0 % HCl concentration, 60˚ C reaction temperature, 5% initial solid loading and 500 rpm mixing speed. Under these conditions sCOD, sRedSugar and BMP were estimated as 590 mgCOD/gVS, 330 mgGlucose/gVS and 275 $mLCH_4/gVS$, respectively. In order to validate the optimization, a specific batch run was performed. In this run, sCOD, sRedSugar and BMP were determined as 615.6 mgCOD/gVS, 330 mgGlucose/gVS and 270 $mLCH_4/gVS$, proving fair predictive power of the model.

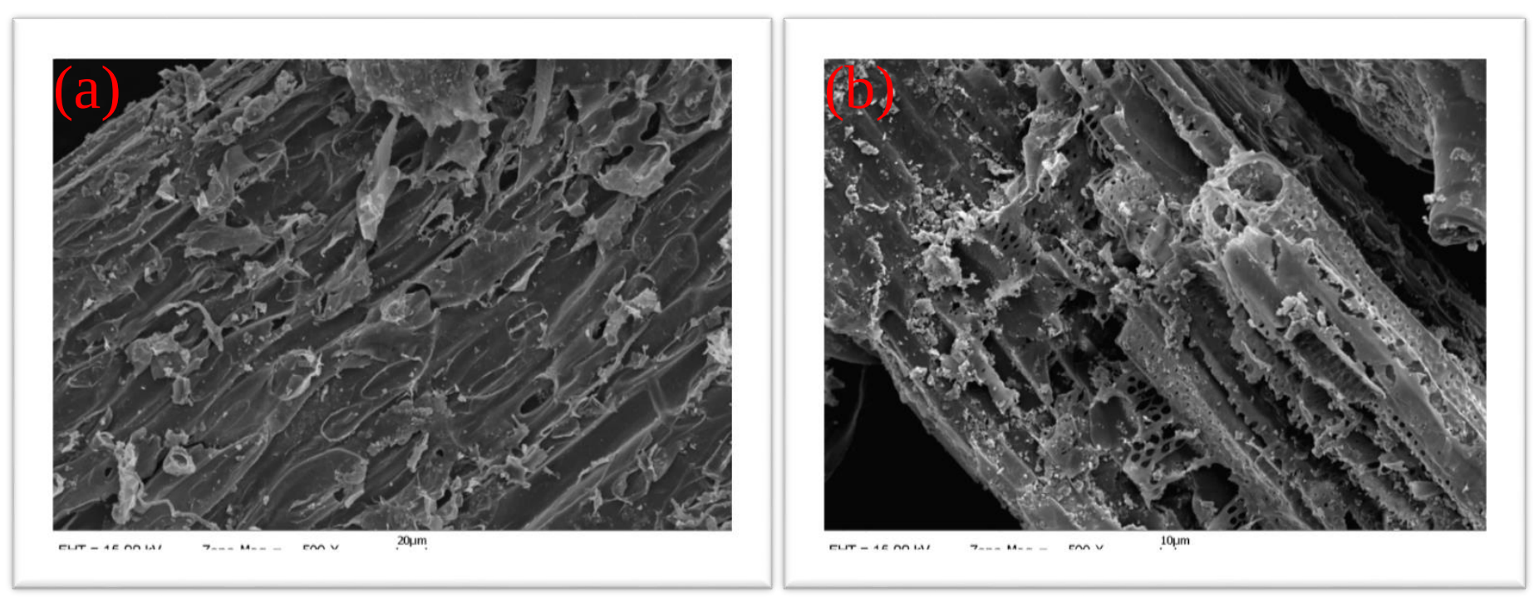


Figure 2. SEM images

SEM images of untreated raw GHR and pretreated GHR at optimized conditions are presented in Fig. 2 (a) and (b), respectively. SEM image of untreated raw GHR exhibited rigid, smooth and continuous surface, whereas fibrils of pretreated material are separated from the main structure and exposed.

CONCLUSIONS

- •Effects of thermal HCl pretreatment for the enhancement of biogas production from GHR were investigated.
- •BMP of raw GHR was found as 217 $mLCH_4/gVS$.
- •A cost driven approach and production of maximum BMP were preferred in the optimization. Optimum conditions were obtained as 0% HCl concentration, 60°C reaction temperature, 5% initial solid loading and 500 rpm mixing speed. Under these conditions BMP was measured 270 $mLCH_4/gVS$ and increase in BMP (%) is calculated as 24.4%.

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