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Research article

# Effect of thermal pretreatment on chemical composition, physical structure and biogas production kinetics of wheat straw

Asad Ayub Rajput[a], Zeshan[a,*], Chettiyappan Visvanathan[b]

[a] Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan

[b] Environmental Engineering and Management, School of Environment, Resources and Development, Asian Institute of Technology, Bangkok, Thailand

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ABSTRACT

Hard lignocellulosic structure of wheat straw is the main hindrance in its anaerobic digestion. Thus, a laboratory scale batch experiment was conducted to study the effect of thermal pretreatment on anaerobic digestion of wheat straw. For this purpose, different thermal pretreatment temperatures of 120, 140, 160 and 180 °C were studied and the results were compared with raw wheat straw. Significant differences in biogas production were observed at temperature higher than 160 °C. Highest biogas yield of 615 Nml/gVS and volatile solids reduction of 69% was observed from wheat straw pretreated at 180 °C. Wheat straw pretreated at 180 °C showed 53% higher biogas yield as compared to untreated. Further, FTIR analysis revealed change in chemical bonds of lignocellulosic structure of wheat straw. Modified Gompertz model was best fitted on biogas production data and predicted shorter lag phase time and higher biogas production as the pretreatment temperature increased. Overall, change in lignocellulosic structure and increase in cellulose content were the main reason in enhancing biogas production.

## 1. Introduction

Energy is a vital element for continued economic growth and development. Unfortunately, Pakistan is facing numerous problems due to energy deficiency. To overcome severe power crisis the country is looking for different renewable and sustainable energy options. In this scenario bioenergy can play a crucial role since bioenergy is considered as fourth largest energy resource in the world. Enormous source of agricultural biomass is available for bioenergy production in Pakistan. It is estimated that the country generates around 69 million tons of field based agricultural crop residues annually (Raheem et al., 2016). Wheat straw is one of crop residue types produced in huge quantities from agricultural fields. Pakistan produces approximately 25 million tons of wheat straw every year (Arshadullah et al., 2012).

Anaerobic digestion of wheat straw could be a promising way of bioenergy production as it reduces various problems originated from its inadequate disposal. However, the process consists of many stages including hydrolysis, acidogenesis and methanogenesis, out of which hydrolysis is considered as the rate-limiting step in anaerobic digestion of wheat straw due to its lignocellulosic nature. In a lignocellulosic biomass like wheat straw, the connected structure of lignin and hemicellulose provides physical barrier to degradation of cellulose and hence limits its biodegradation rate. Thus, suitable pretreatment is required to enhance digestibility of lignocellulosic wheat straw.

Various pretreatment methods are used for increasing the anaerobic digestibility of lignocellulosic waste. These include dilute acid pretreatment (Schell et al., 2003), mechanical pretreatment for size reduction (Mshandete et al., 2006), microbial pretreatment (Mustafa et al., 2016) and microwave pretreatment (Sapci, 2013). These pretreatments alter the lignocellulosic structures by breaking the chemical bonds, which may increase the potential of cellulose hydrolysis and biogas production (Fang et al., 2015; Jaffar et al., 2016; Wang et al., 2016). However, there are certain limitations in the use of these pretreatments. For instance, chemical pre-treatment produces secondary pollution and biological pre-treatment conditions are difficult to control, and combined pre-treatment usually has the disadvantages of both chemical and biological methods. In comparison, physical pre-treatment methods are most commonly used due to operational convenience and low investment (Haghighi Mood et al., 2013).

Thermal pretreatment is a type of physical pretreatment in which the lignocellulosic biomass is subjected to heating at a certain temperature and pressure. The temperature range for this purpose could be 50–240 °C. Depending on the type of heating method, it could be called as thermal pretreatment, hydrothermal pretreatment, steam explosion

* Corresponding author.
*E-mail addresses:* zeshansheikh@iese.nust.edu.pk, zeshan90@gmail.com (Zeshan).

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**Table 1**
Overview of effect of thermal pretreatment on AD of lignocellulosic biomass.

| Biomass | Pretreatment | Pretreatment conditions | Findings | References |
|---|---|---|---|---|
| Wheat straw | Thermal pretreatment | 150–220 °C for 1–15 min | 20% increase in methane production | Ferreira et al. (2013) |
| Wheat straw | Steam explosion | 180 °C for 15 min | Increased 20% methane yield | Bauer et al. (2009) |
| Washed vinegar residue | Hydrothermal pretreatment | 80, 120 and 160 °C for 30 min | 160 °C pretreated biomass showed 55.99% higher methane yield | Ran et al. (2018) |
| Rice straw | Hydrothermal pretreatment | 90, 150, 180 and 210 °C for 15 min | 3% increase in biogas yield at 90 and 180 °C and 30% decrease at 210 °C compared to control | Wang et al. (2018) |
| Urban and industrial waste activated sludge | Thermal Pretreatment | 60, 80, 100, 120 °C for 30 min | Increased in biogas yield of 27 and 37% at 120 °C | Ennouri et al. (2016) |
| Dewatered sludge | Thermal Pretreatment | 160 °C and 0.55 Mpa for 30 min | 45.7% increase in biogas production | Chen et al. (2018) |
| Wheat straw and sugarcane bagasse | Thermal pretreatment | 121 °C for 60 min | 29% increase in methane production from wheat straw and 11% from sugarcane bagasse | Bolado-Rodríguez et al. (2016) |

or microwave heating (Table 1). Menardo et al. (2012) studied the effect of thermal pretreatment on anaerobic digestion of wheat, barley and rice straw and maize stalk at pretreatment temperature of 90 and 120 °C for 30 min and found 64.2, 40.8, 32.4 and 7.1% increase in methane yield respectively at 120 °C compared to untreated control. Similarly, hydrothermal pretreatment of wheat straw at 200 °C for 10 min showed 20% increase in methane yield (Chandra et al., 2012). Another study reported 27% increase in methane yield from thermally pretreated wheat straw at 200 °C for 5 min as compared to control (Ferreira et al., 2014). Most of the studies mentioned here and in Table 1 used high temperature with a short pretreatment time. On the other hand, a relatively long pretreatment time of 60 min at lower pretreatment temperatures of 60, 70, 80, 90 and 100 °C has been used in a recent study (Chen et al., 2017) for thermal pretreatment of textile dying sludge, in which the highest methane yield was produced from the sludge pretreated at 100 °C. Thus, effect of thermal pretreatment of wheat straw at medium temperatures and long residence time on biogas production has not been studied before and it may produce new information in the area.

Mathematical kinetic models play vital role in design and optimization of any process (Batstone, 2006). To assess the performance of anaerobic digestion (AD) process, several kinetic models have been used by researchers, which include Chen and Hashimoto model (Chen and Hashimoto, 1980), Monod model (Zamanzadeh et al., 2013), first order model (López et al., 2015), substrate mass balance model (Zhang et al., 2015), and modified Gompertz model (Syaichurrozi and Sumardiono, 2013). Modified Gompertz model is considered very efficient in explaining lag phase time and sigmoidal growth curves (Pham et al., 2014) of methane production. As pretreatment of biomass affects lag phase time of the anaerobic process, it could be well explained by Gompertz model. The proposed kinetic models would be helpful to address the theoretical contextual for AD experimental data and hence the effectiveness of the applied pretreatment.

The overall objective of the study is to assess the effect of thermal pretreatment on the biogas production of wheat straw. In addition, chemical and structural changes due to thermal pretreatment were also studied. Further, biogas production rate was assessed in relation to various thermal pretreatment temperatures by using experimental data with the help of three different kinetic models.

## 2. Materials and methods

### 2.1. Inoculum and substrate

Digested manure was used as an inoculum in the study. Fresh digested manure, collected from local biogas plant, was sieved to obtain a uniform particle size of less than 2 mm and pre-incubated under anaerobic conditions at 35 °C for 14 days to remove residual organic matter. Wheat straw was used as a substrate and collected from local farmer near the study area.

### 2.2. Thermal pretreatment

The thermal pretreatment of wheat straw was performed in a 250 mL stainless steel reactor with an inserted Teflon box. In Teflon inserted reactor, 80 g sample of wheat straw was taken, and 20 g of distilled water was added into it to avoid burning of dry biomass during pretreatment. The stainless-steel reactor was fully tightened and placed in a high temperature box resistance furnace – x series (SX-5-12, China). Thermal pretreatment temperatures were set at 120, 140, 160 and 180 °C, and after 60 min of thermal pretreatment the reactor was cooled down using cold water. Finally, the pretreated wheat straw samples at different temperatures were dried and stored in a vacuum plastic bag until use. Thermal pretreatment of wheat straw was performed in triplicate.

### 2.3. Batch anaerobic digestion experiments

In this study, wheat straw pretreated at four different thermal pretreatment temperatures was compared for biogas production. Serum bottles of 300 mL with working volume of 225 mL were used as batch reactors. Calculated quantities of substrate and pre-incubated inoculum (20% of working volume) were taken in reactors to achieve the organic loading of 10 gVS $L^{-1}$ at substrate to inoculum (S/I) ratio of 1 (on gVS basis). After taking the substrate and inoculum, the reactors were flushed with nitrogen gas for ensuring anaerobic condition. The reactors were tightly closed with rubber stopper and alumina crimp cap and placed in an incubator at 35 °C for 45 days. Mixing was provided to every reactor twice a day for 2–3 min. A glass gas syringe was used to measure daily biogas production from reactors. No external nutrients were added, all the required nutrients were provided by fresh inoculum (digested manure). The experiment was carried out in triplicate. To get the biogas production from untreated substrate, control reactor of untreated wheat straw was also prepared and run. Therefore, five sets of reactors were prepared viz., untreated wheat straw, pretreated wheat straw at 120, 140, 160 and 180 °C.

### 2.4. Analytical parameters

Analyses for total solids (TS), volatile solids (VS) and total kjeldahl nitrogen (TKN) of wheat straw before and after pretreatment were carried out according to standard methods (APHA, 2005). Total organic carbon (%TOC) was calculated by dividing the value of volatile solid content (%VS) with a factor of 1.8 (Adams et al., 1951). Biogas was collected in gas collection bags and methane content in biogas was analyzed using gas analyzer (Biogas 5000, Geotech, UK).

Lignin, hemicellulose and cellulose contents in different wheat straw samples were measured with the help of chemical method as described in Li et al. (2004). The detail of the analysis is as follows. First, the amount of extractives in the biomass was determined by using solvent extraction, for which, 60 mL acetone was used for 1 g of dried