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Chemical Pretreatments of Rice Straw for Anaerobic Digestion

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Abstract

Rice (*Oryza sativa*) is an important staple food for approximately half of the world population. In addition to the grains also the straw can be used if not needed as organic fertilizer for the fields. Although rice straw has potential to be used for anaerobic digestion (AD) to produce biogas, its large scale application is still limited. The utilization of rice straw for AD must particularly be developed regarding the pretreatment of the lignin biomass for the hydrolysis process and the biogas yield and quality. Among the pretreatment methods, the alkalization method was found to be effective. In the present study the effects of rice straw pretreatment were investigated in a multifactorial approach. For this purpose, calcium hydroxide ($Ca(OH)_2$) and potassium hydroxide (KOH) were applied at different concentrations. Furthermore, the reaction time and inoculum-to substrate ratio were included in the investigations. Results showed that the degradation of lignin, cellulose, and hemicellulose was higher after the chemical pretreatment. The main end-products identified were acetic and propionic acids. The highest hydrolysis yield was observed at a reaction time of 4 h, with an alkali concentration of 10 g per g rice dry matter, and an inoculum-to-substrate ratio of 50%. Here also the maximum concentration of volatile fatty acids was observed with 187±30 mg L^{-1}. The composition of the acidified effluent was similar when both chemical compounds were used. Economically, the optimal amount of $Ca(OH)_2$ for the pretreatment of rice straw was 4 g per g rice dry matter. The results showed, that the additional effort of a pretreatment of rice straw can be worthwhile to improve the AD and to increase the biogas yield.

Keywords: Bioenergy, biogas, biomass, digestion

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Introduction

Rice straw is one of the most abundant renewable lignocelluloses crop residues (LCR) with the most availability in the world. Rice Straw is commonly used for animal feed and as a fuel for cooking and heating homes. However, the largest amounts of rice straw remain unused in the field and burned in the open fields causing serious environmental problems. (Shetty et al. 2016). Anaerobic digestion (AD) to produce biogas can offer promising benefits for using rice straw and mitigating air pollution. It has been confirmed that AD is an attractive technology for simultaneous clean bioenergy production and waste treatment. Biogas and digestate are the two beneficial products of AD. Digestate is rich in nitrogen and organic matter and can be used in agriculture as a biofertilizer or soil improver (Guan et al. 2018). However, the inherent characteristics of rice straw made it resistant to enzymatic degradation by anaerobic microbes. For that reason, pretreatment of rice straw prior to AD process has been proven to be necessary to improve biodegradability and biogas production. Chemical pretreatment has been defined as the most promising method to improve the bioconversion of cellulose in order to improve the enzymatic accessibility and thus facilitate the subsequent anaerobic treatment (Sabeeh et al. 2020). Various pretreatment protocols have been used for the biomethanation of rice straw that involve heating and the use of various amounts of chemicals (Kim et al. 2018). However, alkali pretreatments are commonly investigated at elevated temperature (over 100°C) with the drawbacks of special equipment requirement, higher treatment costs and high energy consumption (Dong et al. 2018). Hence, the major objective of the present investigation was to minimize the alkali requirement at low temperature during pretreatment to enhance the hydrolysis of rice straw. In the present study the effects of rice straw pretreatment were investigated in a multifactorial approach. For this purpose, calcium hydroxide ($Ca(OH)_2$) and potassium hydroxide (KOH) were applied at different concentrations.

Material and Methods

Rice straw was air-dried and milled using hammer mill grinder and sieved to select straw of desired particle size. The cellulose, hemicellulose and acid-insoluble lignin content in the rice straw sample was determined by the Van Soest method (Van Soest et al. 1991). The detection of total solids (TS) and volatile solids (VS) was carried out in accordance with the standard methods of APHA (APHA 1995). Slurry obtained from a cow dung biomethanation industrial plant operated at 37 ^{o}C was used as an inoculum for hydrolysis from rice straw. The pH of the inoculum was 7. To study the best conditions of hydrolysis of rice straw residues, a factorial experimental design was used. Four experimental factors were considered: type of alkali compound ($Ca(OH)_2$, KOH), time of reaction (2, 3, and 4 h), concentration of alkali compound (4, 7, and 10 g/g dry matter), and inoculum-to-substrate ratio (20, 35, and 50 %). In tests designed, 4 g of rice straw was added to 100 mL of each alkali solution during the corresponding pretreatment time and kept at 35 ºC with circulating water. Then, the alkali solution was drained and the corresponding inoculum-to substrate ratio was added to each bottle and subsequently made up to volume with water to a volume of 100 mL. All tests were performed at 35 ° C using 250 ml borosilicate glass reactors with 100 ml working volume, at an initial pH of 7.0. An untreated sample of rice straw was simultaneously tested as the control. Each experiment was performed for 10 days. VFA samples were prepared by centrifuging at 13000 rpm for 5 min before filtering through a 0.2 µm nylon membrane. VFA concentrations were measured using a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a flame ionization detector (FID).

Results and Discussion

Composition of rice straw

Rice straw, like many lignocellulosic biomasses, possess several properties that makes them suitable as feedstocks for bio-chemical conversion. Table 1 shows the chemical characteristics of the rice straw used in this study. The results showed that the rice straw was composed of 48.7% cellulose, 22.2% hemicellulose, and 3.1% lignin. Thus the rice straw was considered as a promising carbon source for microbial fermentation. On the another hand, rice straw contained 90.3% (w/w) total solid; meanwhile, volatile solids constituted 77.5% of the TS.

Table 1. Characteristics of rice straw

Celulose (%)	Hemicellulose (%)	Lignin (%)	pH	TS (%)	VS (% of TS)	Na (mg/L)	K (mg/L)
48.7	22.2	3.1	6.42	90.3	82.1	10	150
P (mg/L)	**Ca (mg/L)**	**Cd (mg/L)**	**Cr (mg/L)**	**Cu (mg/L)**	**Mg (mg/L)**	**Ni (mg/L)**	**Pb (mg/L)**
37.5	35.9	0.017	0.023	0.053	17.6	0.047	1.06

Effect of pretreatments on hydrolysis process

Alkali pretreatment is capable of improving rice straw biodegradability by releasing organic soluble fraction. A fixed quantity of rice straw was exposed to various concentrations of Ca(OH)2 and KOH for varying duration to optimize the pretreatment at low temperature. The efficacy of the pretreatment on the hydrolysis stage was monitored in terms of VFA production. The VFA concentrations of the pretreated rice straw is shown in Fig. 1.

$Ca(OH)_2$	KOH

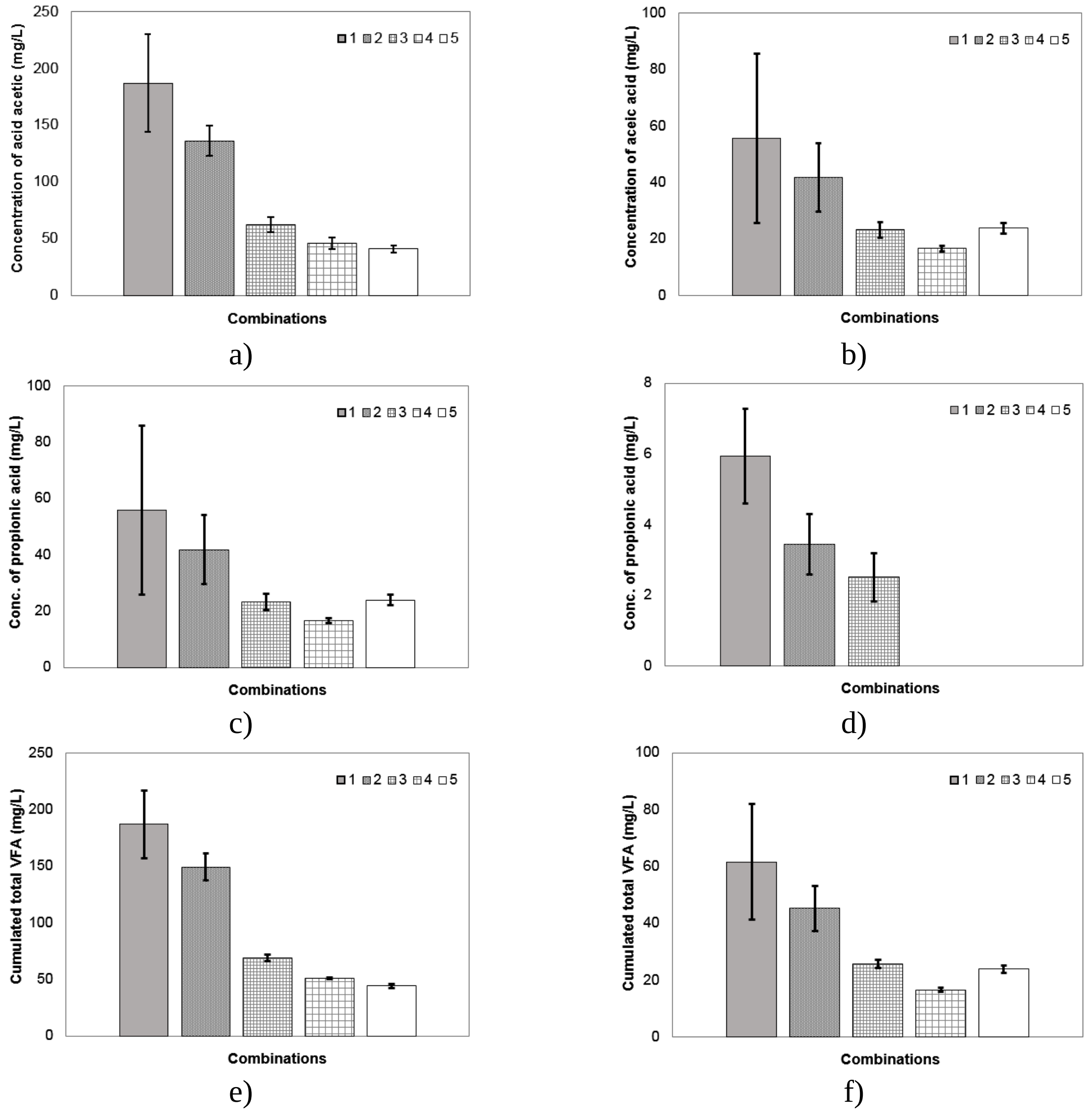

Fig. 1. VFA concentration of pretreated rice straw; a) and b) acetic acid; c and d) butyric acid; and e) and f) cumulated total VFA.

VFA in the anaerobic reactors mainly comprised acetic and propionic acids. No significant accumulation of butyric and iso-butyric acids was observed, probably because of the sufficient butyric-degrading syntrophs in the inoculum, which rapidly converted these acids to acetic acid. Total VFA production increased from 89±12 mg/L for untreated rice straw to 187±30 mg/L when rice straw was pretreated for 4 hours with 10 g per g rice dry matter of $Ca(OH)_2$ and used an inoculum-to-substrate ratio of 50 %. Compared to KOH, the $Ca(OH)_2$ had more significant influence on the VFA production. ANOVA confirmed that the both concentration of alkali compounds significantly ($p< 0.05$) influenced the production of VFA. Economically, the optimal amount of $Ca(OH)_2$ for the pretreatment of rice straw was considered 4 g per g rice dry matter due to not significant differences were observed at dose of 10 g per g rice dry matter. Hence, for further investigation, rice straw will pretreat with 5% (g/gTS) $Ca(OH)_2$ for 4 hours at 35 ºC temperature and evaluated for biomethanation. The preliminary results suggested that from the same amount of raw material loaded, the pretreated rice straw with $Ca(OH)_2$ the hydrolysis yield is highest compared with untreated rice straw.

Conclusions and Outlook

The results of this study show that $Ca(OH)_2$ pretreatment could significantly enhance the hydrolysis of milled rice straw. Maximum production of VFA (187 mg/L) was achieved with rice straw treated with 10% $Ca(OH)_2$ at 35 ºC temperature for 4 hours. Alkali pretreatment increased the production of VFA by 47% over that obtained with milled rice straw without alkali treatment. $Ca(OH)_2$ pretreatment is a promising pretreatment process that can be carried out at low temperature.

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